Liquid carbon dispersions for energy applications

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Abstract

The aim of this work is to develop and study a new class of smart fluids made of colloidal carbon-based dispersions, which are sensitive to an external stimulus for energy storage or conversion applications. The effect of an external input, such as mechanical vibration, human motion, variable pressure, flowing of a solvent, can alter the structures of such systems. Consequently these changes induce modifications of the dielectric and electrical properties. Usually, the suspensions of carbon materials are investigated at rest or dried. However, their flow behavior is critical when new technologies, which exploit these materials in dynamic conditions such as FAES (Flow-Assisted Electrochemical Energy Storage) are considered. For example, graphene-based materials are now playing a significant role in energy materials. They act as conductive additives in electrode assemblies, but due to their specific anisotropic shape they also provide a new route to achieve dielectric liquid media.

In details, Graphene Oxide liquid crystals as electrostrictive soft material for mechanical energy harvesting and Carbon black dispersions as percolated flowable electrodes for capacitive energy storage are investigated.

In particular, the dielectric and electrical properties of these flowable dispersions are studied under static and dynamic conditions. The effect of the flow-rate on the local orientation and reorganization of the particles and their related dielectric and electrical behavior are examined.
Résumé

De la révolution industrielle à la fin du siècle dernier, la production d'énergie reposait sur des combustibles fossiles (charbon, gaz naturel et pétrole). Actuellement, l'économie mondiale dépend fortement de ces ressources. Pourtant la pénurie imminente des combustibles fossiles, les tensions internationales provoquées par leur approvisionnement et les changements climatiques dus à l'émission de gaz à effet de serre dans l'atmosphère mettent l'économie mondiale au défi de trouver des sources d'énergie alternatives. Il était également nécessaire de trouver un moyen plus efficace pour stocker l'énergie. Depuis le protocole de Kyoto, les grandes puissances mondiales ont signé des traités internationaux pour réduire drastiquement les émissions de gaz à effet de serre dans les années à venir. Pour cela, de nouvelles technologies basées sur "l'énergie verte", telles que l'énergie hydroélectrique, géothermique, éolienne et solaire ont été développées.

Au cours des dernières années, le développement de nouvelles méthodes efficaces pour la production d'énergie verte à partir de ressources renouvelables a suscité un vif intérêt. Cependant, l'efficacité de l'alimentation en énergie provenant de ces sources n'est toujours pas satisfaisante compte tenu de leur variabilité et de leur accessibilité discontinue. Le seul moyen d'augmenter leur performance est de les combiner avec des systèmes de stockage d'énergie appropriés.

Les systèmes de stockage d'énergie sont nécessaires pour pallier à certains défauts de l'électricité (les variations horaires de la demande et du prix par exemple) et pour en assurer la distribution. Le recours à des ressources renouvelables pour réduire les émissions de CO₂ rendra les systèmes de stockage d'énergie encore plus essentiels dans un avenir proche. Ces systèmes jouent trois rôles principaux: ils permettent de réduire les coûts d'électricité en stockant l'électricité produite pendant les «heures creuses» (lorsque son prix est inférieur), qui sera utilisée à tout moment; ils peuvent fournir de l'énergie lors de tout type de défaillance du réseau électrique, améliorant ainsi la fiabilité de l'alimentation électrique; ils maintiennent et améliorent la qualité de l'énergie, la fréquence et la tension.

Il existe différentes façons de stocker l'énergie selon l'usage que l'on souhaite en faire. En général, il est possible de distinguer deux classes de méthodes de stockage d'énergie: électrique et thermique, elles-mêmes divisées en sous-catégories.
Cette thèse se concentre sur certains aspects de la méthode de stockage d'énergie électrique. Concernant les utilisations stationnaires, les systèmes de stockage d'énergie mécanique et chimique sont préférés. Vis-à-vis des systèmes intégrés, les batteries rechargeables sont plus avantageuses en raison de leurs densités de puissance, de leurs excellentes performances de cycle et de leur poids limité. À l'heure actuelle, les piles rechargeables et les supercondensateurs restent les solutions les plus pratiques. Ils jouent donc un rôle essentiel dans notre vie quotidienne et il serait souhaitable de les utiliser avec des matériaux nouveaux et plus efficaces.

Les matériaux à base de carbone semblent être de bons candidats à cet effet, comme le soulignent souvent les études récemment consacrées à ce domaine. Ces matériaux peuvent être utilisés non seulement pour la fabrication d'électrodes poreuses, mais aussi comme supports fluides pour le stockage d'énergie mécanique et capacitif. Les matériaux à base de graphène et d'autres matériaux 2D ont un fort potentiel dans les applications liées à l'énergie.

L'objectif de ce travail est de développer et d'étudier une nouvelle classe de fluides intelligents à base de dispersions colloïdales de carbone, sensibles à un stimulus externe pour des applications de conversion et stockage d'énergie. Ces stimuli sont de différentes natures: vibration mécanique, mouvement humain, variation de pression ou écoulement d'un solvant, et peuvent alterer les structures de tels systèmes. Ceci induit une modification de la structure locale des particules et par conséquent des propriétés diélectriques et électriques. Habituellement, les suspensions de matériaux carbonés sont étudiées au repos ou séchées. Toutefois, comprendre leur comportement en flux est essentiel pour de nouvelles applications où ces matériaux sont exploités dans des conditions dynamiques telle que le stockage d'énergie électrochimique assisté par flux (FAES). Par exemple, les matériaux à base de graphène jouent désormais un rôle important dans les nouvelles technologies énergétiques. En effet, ils sont utilisés comme additifs conducteurs dans les assemblages d'électrodes. De plus, dotés d'une forme anisotrope spécifique, ils permettent d'obtenir des fluides diélectriques sous écoulement.

Les cristaux liquides d'oxyde de graphène, en tant que matériau souple électrostrictif, sont étudiés pour la récupération d'énergie mécanique, ainsi que des dispersions de noir de carbone pour le stockage d'énergie.
Les propriétés diélectriques et électriques de ces dispersions fluides dans des conditions statiques et dynamiques sont mesurées et analysées. Enfin, l’effet de l’écoulement sur l’orientation et la réorganisation locale des particules et leur comportement diélectrique et électrique sont examinés.

Le premier chapitre expose tout d’abord les problématiques actuelles en terme de production et de stockage d’énergie électrique. Elles sont également introduites les technologies existantes de stockage d’énergie électrochimique en termes de performances et de limitations des matériaux à base de carbone dans ce secteur. Enfin, ce premier chapitre décrit le principe des supercondensateurs et condensateurs électrochimiques assistés par flux et les concepts associés (densités d’énergie et de puissance, double couche électrique). L’ensemble donne une idée suffisamment claire, complète et convaincante de l’état de l’art, des systèmes et des concepts abordés. Le premier chapitre présente également une vaste et précise bibliographie sur le sujet.

Le deuxième chapitre présente les matériaux et méthodes utilisés. Le montage expérimental pour étudier les propriétés statiques et dynamiques y est présenté en détail. En premier lieu, sont étudiés, les protocoles de préparation des dispersions d’oxyde de graphène et de noir de carbone. Puis sont analysés les méthodes et dispositifs expérimentaux de caractérisation utilisés (microscopie optique polarisée, mesures d’impédance statiques/en flux sous cisaillement, rhéologie, charge - décharge électrique). De manière générale, les deux objectifs principaux de ce chapitre sont la description des détails expérimentaux nécessaires à la reproduction des travaux et l’introduction des concepts théoriques nécessaires à l’interprétation des données.

Le troisième chapitre vise l’utilisation potentielle des cristaux liquides d’oxyde de graphène en tant que matériau souple électrostrictif pour la récupération d’énergie mécanique et les applications de détection. De plus, les mesures diélectriques dépendantes de l’écoulement sont corrélées à une étude de la biréfringence induite par l’écoulement par microscopie optique polarisée. Le chapitre présente le concept de production d’électricité à partir de vibrations mécaniques ainsi que les matériaux associés (électrostrictifs, magnétostrictifs, piézoélectriques). En outre, les concepts de transduction électrostatique en cycle, de relaxation diélectrique (dans le cas d’une phase pseudo-lamellaire de feuillets diélectriques) et d’électrostriction (dans le cas d’une telle phase fluide mise en mouvement) y sont décrits.
Un modèle de type circuit RC est ensuite proposé pour modéliser la réponse en permittivité du système selon l’orientation des feuillets. La capacité et la conductivité expérimentales des phases statiques et en mouvement sont ensuite rapportées. Elles sont combinées avec des mesures de biréfringence pour évaluer les perturbations de l’orientation sous flux et les amplifier en favorisant un flux turbulent.


Les résultats obtenus devraient conduire à une remise en question des méthodes précédemment utilisées pour mesurer la permittivité de phases dispersées. Des études plus approfondies de l’influence des caractéristiques structurales de feuillets bidimensionnels sur leurs propriétés diélectriques seraient nécessaires.

Le cinquième et dernier chapitre est dédié à l’étude de suspensions conductrices de noir de carbone pour le stockage d’énergie assisté par flux pour condensateurs de flux électrochimiques (EFC). Il s’agit d’une nouvelle technologie de stockage d’énergie sur réseau basée sur les principes fondamentaux des supercondensateurs et des batteries à écoulement. Le concept de condensateur électrochimique assisté par flux y est présenté. De même que le besoin associé pour des électrodes fluides de grande surface spécifique et le compromis entre viscosité et conductivité électrique consécutif au phénomène de percolation.
Dans ce chapitre, une étude complète sur les propriétés rhéologiques et électriques de ces dispersions à base de carbone et leur utilisation relative dans des conditions dynamiques est présentée. 

Enfin, sont décrits les travaux expérimentaux combinant optimisation de la phase dispersante et de la concentration en noir de carbone, voltamétrie cyclique, mesures de rhéologie et mesures de charge-décharge électrique (statiques et sous flux).
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<tbody>
<tr>
<td>AC</td>
<td>Alternative current</td>
</tr>
<tr>
<td>CB</td>
<td>Carbon black</td>
</tr>
<tr>
<td>CDI</td>
<td>Capacitive Deionization Water</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DLA</td>
<td>Diffusion Limited Aggregation</td>
</tr>
<tr>
<td>DS</td>
<td>Dielectric spectroscopy</td>
</tr>
<tr>
<td>ECs</td>
<td>Electrochemical capacitors</td>
</tr>
<tr>
<td>EDL</td>
<td>Electric Double Layer</td>
</tr>
<tr>
<td>EDLCs</td>
<td>Electrochemical Double-Layer Capacitors</td>
</tr>
<tr>
<td>EEC</td>
<td>Equivalent Electrical Circuit</td>
</tr>
<tr>
<td>EES</td>
<td>Electrical energy storage</td>
</tr>
<tr>
<td>EFC</td>
<td>Electrochemical Flow Capacitor</td>
</tr>
<tr>
<td>EP</td>
<td>Electrode polarization</td>
</tr>
<tr>
<td>ER</td>
<td>Electrorheological</td>
</tr>
<tr>
<td>ESR</td>
<td>Equivalent Series Resistance</td>
</tr>
<tr>
<td>FAES</td>
<td>Flow-Assisted Electrochemical Energy Storage</td>
</tr>
<tr>
<td>FEs</td>
<td>Flowable electrodes</td>
</tr>
<tr>
<td>FETs</td>
<td>Field Effect Transistors</td>
</tr>
<tr>
<td>FLG</td>
<td>Few Layers Graphene</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene Oxide</td>
</tr>
<tr>
<td>GOLCs</td>
<td>Graphene Oxide Liquid Crystals</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly Oriented Pyrolytic Graphite</td>
</tr>
<tr>
<td>LB</td>
<td>Langmuir-Blodgett</td>
</tr>
<tr>
<td>LIBs</td>
<td>Lithium-Ion Batteries</td>
</tr>
<tr>
<td>MEMS</td>
<td>Micro-Electro-Mechanical Systems</td>
</tr>
<tr>
<td>MR</td>
<td>Magnetorheological</td>
</tr>
<tr>
<td>POM</td>
<td>Polarizing optical microscopy</td>
</tr>
<tr>
<td>RES</td>
<td>Renewable energy sources</td>
</tr>
<tr>
<td>RLA</td>
<td>Aggregation Limited Reaction</td>
</tr>
</tbody>
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### Acronyms and Symbols

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tbody>
<tr>
<td>SAM</td>
<td>Self-Assembly Monolayer</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small Angle X-Ray Scattering</td>
</tr>
<tr>
<td>SMES</td>
<td>Superconducting Magnetic Energy Storage</td>
</tr>
<tr>
<td>SSFC</td>
<td>Semi Solid Flow Cell</td>
</tr>
<tr>
<td>TES</td>
<td>Thermal energy storage</td>
</tr>
<tr>
<td>...</td>
<td></td>
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</tbody>
</table>

- $dV/dt$  
  \text{Scan rate}
- $\phi_V$  
  \text{Volume Fraction}
- $\phi_c$  
  \text{Volume Fraction Critical}
- $\dot{\gamma}(z)$  
  \text{Shear rate}
- $C_{eff}$  
  \text{Effective Capacitance}
- $C_{min}$  
  \text{Charge minimum}
- $|E|$  
  \text{Applied Potential}
- $I_{plateau}$  
  \text{Stabilized Current}
- $P_{in}$  
  \text{Input Pressure}
- $P_{out}$  
  \text{Output Pressure}
- $R_{Leakage}$  
  \text{Resistance leakge}
- $R_c$  
  \text{Resistance charge process}
- $R_d$  
  \text{Resistance discharge process}
- $U_{min}$  
  \text{Potential minumim}
- $V_{in}$  
  \text{Voltage applied to the RC circuit}
- $V_{out}$  
  \text{Voltage across the cell}
- $\varepsilon_{eff}$  
  \text{Effective dielectric constant}
- $\varepsilon_p$  
  \text{Dielectric constant of the particle}
- $\varepsilon_r$  
  \text{Relative permittivity}
- $\varepsilon_s$  
  \text{Dielectric Constant of the solvent}
- $\varepsilon_0$  
  \text{Vacuum permittivity}
- $\sigma(z)$  
  \text{Shear stress}
- $\sigma_e$  
  \text{Electronic conductivity}
- $\sigma_p^*$  
  \text{Complexe conductivity of the particle}
\( \sigma_s^* \)  Complexe Permittivity of the sample  
\( \sigma_0 \)  Yield stress  
\( \tau_0 \)  Relaxation time  
\( v_{(x)} \)  Velocity  
\( \phi_c \)  Volume fraction critical  
\( A \)  Surface area  
\( C \)  Capacitance  
\( C_{\text{bulk}} \)  Capacitance of bulk of dispersion  
\( C_{\text{dl}} \)  Capacitance of electric double layer  
\( C_{\text{max}} \)  Charge maximum  
\( C_{\text{min}} \)  Charge minimum  
\( C_p \)  Capacitance particle  
\( C_s \)  Capacitance of solvent  
\( d \)  Distance  
\( e \)  Thickness of the channel  
\( L \)  Length of anisotropic particles  
\( N \)  Director of liquid crystal  
\( Q \)  Electric Charge  
\( Q_{\text{cst}} \)  Charge constant  
\( R \)  Resistance  
\( R \)  Width of anisotropic particles  
\( RC \)  Resistor-Capacitor Circuit  
\( R_{\text{disp}} \)  Resistance of dispersion  
\( R_p \)  Resistance of the particle  
\( R_{\text{pol}} \)  Resistance of the polarization of electrode  
\( R_s \)  Resistance of solvent  
\( t \)  Thickness of the solvent layer  
\( U \)  Potential  
\( U_{\text{max}} \)  Potential maximum  
\( W \)  Warburg element
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$Z^*$</td>
<td>Complex impedance of the system</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>Thickness of the particle layer</td>
</tr>
<tr>
<td>$L$</td>
<td>Channel length</td>
</tr>
<tr>
<td>$i$</td>
<td>Current</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>Pressure variation</td>
</tr>
<tr>
<td>$\Delta \varepsilon$</td>
<td>Amplitude of relaxation</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Flow index</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Frequency</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Consistency index</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Volume Fraction of the particle</td>
</tr>
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Preface
Preface

From the industrial revolution to the end of the last century, the production of energy relied on fossil fuels (coal, natural gases and oil, for instance). Currently, the global economy strongly depends on these resources, but their forthcoming shortage, the international tensions caused by their supply and the climate changes due to the emission of greenhouse gases in the atmosphere challenge the global economy to find alternative sources of energy and to develop a more efficient way to store energy. Since the Kyoto protocol, the great world powers signed international treaties in order to drastically reduce, in the coming years, the emission of greenhouse gases by developing new technologies based on “green energy”, such as hydro, geothermal, wind and solar energy that have a lower impact on the environment.

In recent years, there has been a strong interest in the development of new and efficient methods for green energy generation from renewable resources that are able to meet the level of the global demand. However, the efficiency of the power supply from these sources is still unsatisfying, given their variability and discontinuous accessibility. The only way to increase their performance is to combine them with appropriate energy storage systems.

Energy storage systems are necessary to overcome some of the critical characteristics of electricity, like hourly variations in demand and price, and make the energy distribution level independent of these criticalities. Switching to renewable sources to reduce CO₂ emissions will make energy storage systems even more essential in the near future. These systems play three main roles: they reduce electricity costs by storing electricity generated during “off-peak times” (when its price is lower), to be used then at any desired time; they can provide energy during any kind of power network failures, improving the reliability of the power supply; they maintain and improve the power quality, frequency and voltage.

There many different solutions for the storage of energy and the selection of one over another mainly depend on the final application. In general, it is possible to distinguish two classes of energy storage methods: electric and thermal, which in turn have different subcategories. This manuscript focuses only on some aspects of the electric energy storage method. For stationary uses, mechanical and chemical energy storage systems are preferred, whereas for embedded systems, rechargeable batteries presents are more advantageous because of their high power/energy densities, excellent cycle performance and their limited
weight. However, the energy storage technology for stationary uses is not within everyone’s means yet, commercially speaking. Currently, rechargeable batteries and supercapacitor are still the most convenient solutions, and for this reason, they play an essential role in our daily life and there is a strong interest to implement them with new and more efficient materials. Carbon-based materials seem to be good candidates for this purpose and for a wide range of applications, as often pointed out by the several studies recently devoted on the field. Carbon-based materials can be used not only for the production porous electrodes, but also as flowable media for mechanical and capacitive energy storage, given the great potential of graphene-based materials and other 2D materials in energy related application.

The objective of this work is focused on the study of the electrical and dielectric properties of liquid carbon-based dispersions for their potential use in energy storage or energy conversion systems. Energy conversion includes energy harvesting and sensing. In details, it will be shown how carbon-based dispersions can be used for both mechanical energy harvesting and capacitive storage, exploiting the behaviour of these materials in static and dynamic conditions.

The first chapter of this thesis will present the state of the art of electrochemical energy storage systems and the current use of carbon-based materials in this sector. The second chapter will be dedicated to the materials and method used in this thesis. In details, the experimental set-up to studies the static and dynamic properties will be presented.

The third chapter will be dedicated to the study of potential use of Graphene Oxide liquid crystals (GOLC) as an electrostrictive soft material for mechanical energy harvesting and sensing applications. In addition, the flow-dependent dielectric measurements will be correlated with a study of flow-induced birefringence through polarized optical microscopy (POM).

The fourth chapter will be dedicated to the potential use of Graphene Oxide liquid crystals (GOLC) as dielectric fluid. In details, the chapter will also highlight the limits of capacitance measurements in two-plates parallel system in the evaluation of the dielectric properties of fluids due to the strong polarization of the electrodes. To overcome this effect, an equivalent electrical circuit model will be proposed to distinguish between the interfacial and bulk properties of such dispersions.
The fifth chapter will be focused on the implementation of an aqueous carbon liquid electrode for electrochemical flow capacitors (EFC), a new technology for grid energy storage based on the fundamental principles of supercapacitors and flow batteries. In this chapter, a complete study on the rheological and electrical properties of these carbon-based dispersions and their relative use in dynamic conditions will be presented.
Chapter I

Carbon-based materials for energy storage
1.1 – Introduction

The shortage of fossil fuels and the increasing pollution due to greenhouse gas emissions are ones of the main problems of modern society. In the last decades, a lot of effort has been done in order to find efficient solutions. Renewable energy sources (RES), such as wind and solar energy, are very promising alternatives to fossil fuels and their integration into the existing utility net systems would help overcoming the dependences on fossil fuels and reduce the emissions of greenhouse gases \cite{1}.

However, the variability and irregular accessibility of these energy sources make their daily life applications still challenging. In fact, a direct consequence of this issue is that the energy supply would not be constant over time, causing periods of power outage during which the end users cannot use electric devices.

One of the possible solutions to this problem is the development of efficient energy storage systems that are capable to store a significant amount of energy and then redistribute it to the users when needed \cite{2-5}. In addition to this obvious advantage, the introduction of energy storage systems in the energy production and distribution network has many other positive implications. It increases the efficiency of power stations, by storing the electricity produced in excess, thus limiting energy wastes \cite{6} and improving the electrical net stability and reliability. Due to their ability to address the fluctuations of demands, it lowers the risks associated with energy security and quality, by maintaining frequency and voltage values that meet the users’ demand, and thus ensuring reliability of supply \cite{7,8}.

There are different technologies used for energy storage, which vary according to the final purpose. In general, these technologies can be broadly classified in two classes: electrical energy storage (EES) and thermal energy storage (TES). The latter, based on the conversion energy from the heat, which can occur in the form of solar or geothermal heat, will not be treated among the topics of this manuscript. Electrical energy is regarded as one of the most readily available form of energy. Currently this resource is considered as a common good and its use is second only to the oil exploitation. Electrical energy needs to be converted into a stable form energy with the intent of transforming it back to electricity when it is required.
There are several technologies that can be used to convert electricity to other forms of energy, which can easily be stored. These technologies are regarded as electrical energy storage technologies and can be grouped as follows: mechanical energy harvesting (Flywheel, Pumped Hydro, Compressed Air and Liquid Piston), chemical energy storage (biofuel cell, hydrogen), electrochemical energy storage (supercapacitors and batteries), and superconducting magnetic energy storage (SMES).

Over past decade, with the optimization of new generation of rechargeable batteries, even electrochemical systems have started to be extended to the massive storage. In specific, the redox-flow batteries have proved to be the right compromise for an electrochemical mass storage system [9,10]. Nevertheless, both fuel cell and redox flow system has not reached yet adapt commercial conditions and nowadays the most convenient way for the electrical energy storage remains the use of supercapacitors and rechargeable batteries [11-13].

1.2 – Electrochemical Energy Storage

All of the energy sources that could be used to produce electrical energy, show large energy losses in average superior of 50%, during the conversion processes. Moreover, given the enormous demand for electricity, its production must be timely and above demand [14]. As previously mentioned a crucial step toward this direction would be the development of systems that are able to accumulate electrical energy to meet the actual energy needs, satisfy the several requests of portable electronic devices or just power simple autonomous sensor network or wireless system [15]. This can be achieved by using electrochemical storage systems; batteries, fuel cells and electrochemical capacitors (ECs).

Despite being based on different storage and conversion mechanisms, electrochemical energy storage systems present some similarities. For example, their architecture generally consists of two electrodes in contact with the electrolyte. However, depending on the nature of the process occurring at the interphase, the accumulation and conversion of energy can be different [16]. One of the main differences between batteries, fuel cells and electrochemical capacitors is the way electricity is generated.
In batteries and fuel cells, faradic processes at the electrodes are responsible for energy production. Differently, in electrochemical capacitors the electrical energy is produced by a non-Faradic process, through the formation of an electric double layer associated to the adsorption of the electrolyte ions at the interface of the electrodes.

The performance of various energy storage devices can be compared by plotting their specific energy densities values (in Wh/Kg) against their specific power density (W/Kg). This kind of diagram is known as Ragone’s plot and it is represented in Figure 1.1. The specific energy density represents the ability of a system to store energy, whereas the specific power density expresses the ability to deliver it. For example, an ideal system should be able to store a significant amount of energy and release it instantly for unlimited number of cycles. This would mean showing a high energy density and a high power energy density. In terms of energy density, the dielectric capacitors show a very low value, less than 1% of the supercapacitors but by other hand, the power density is very high, this means that these devices are able to deliver or accept high currents, but only for short times, due to their relatively low capacitance.

![Ragone’s plot of the principal electric and electrochemical energy storage systems. Power densities (W/kg) of various energy storage devices versus their energy densities (Wh/Kg)\(^{17}\).](image)

Unlike, the supercapacitors show higher energy density than dielectric capacitors but lower values of energy density. However, their cycle life is virtually unlimited and their energy efficiency rarely drops below 90%.
Furthermore, unlike other energy storage systems, such as rechargeable batteries or fuel cells, almost all the energy stored by these systems is available in a reversible process. Depending on the final application, one of the devices could be preferred over the others. At the present, batteries and supercapacitors have found more applications and therefore a higher market demand \(^{[18]}\). Another classification can be made by considering the time that the device needs to store energy. In that perspective, devices can be divided in short and long-term. Usually, batteries are the long-term and the capacitors are the short-term ones. The batteries display a high energy density (in the order of 8 - 600 Wh/Kg) but at the same time, a low power density (typically lower than 500 W/Kg) due to the slow motions of the charge carriers. This is why they are mainly used for long-term and stable energy supply. More detailed characteristics of the electrochemical energy storage systems are presented in the Table 1.1.

<table>
<thead>
<tr>
<th></th>
<th>Dielectric Capacitors</th>
<th>Supercapacitors</th>
<th>Batteries</th>
<th>Fuel Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Charge/Discharge</strong></td>
<td>Ps - ms</td>
<td>ms - s</td>
<td>1 - 10 h</td>
<td>&gt; 10 h (refuel)</td>
</tr>
<tr>
<td><strong>Operating Voltage</strong></td>
<td>6 – 800 V</td>
<td>0.2 – 1V (aqueous)</td>
<td>1.25 to 4.2 V</td>
<td>0.6 V</td>
</tr>
<tr>
<td></td>
<td>2.1 – 3V (organic)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Capacitance</strong></td>
<td>10 pF - 2.2 mF</td>
<td>100 µF – 1500 F</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Power Density</strong></td>
<td>0.25 - 10000 KW/Kg</td>
<td>10 - 120 KW/Kg</td>
<td>0.005 - 0.4 KW/Kg</td>
<td>0.001 - 0.1 KW/Kg</td>
</tr>
<tr>
<td><strong>Energy Density</strong></td>
<td>0.01 - 0.05 Wh/Kg</td>
<td>1 - 10 Wh/Kg</td>
<td>8 - 600 Wh/Kg</td>
<td>300 - 3000 Wh/Kg</td>
</tr>
<tr>
<td><strong>Life</strong></td>
<td>&gt;100000 cycles</td>
<td>Unlimited cycles</td>
<td>150 - 1500 cycles</td>
<td>1500 - 10000 h</td>
</tr>
<tr>
<td><strong>Weight</strong></td>
<td>1g to 10kg</td>
<td>1 g to 230g</td>
<td>1g –10kg</td>
<td>&gt;5kg</td>
</tr>
</tbody>
</table>

Table 1.1 - Brief summary of some critical properties of each electrochemical energy storage devices. The values concerning the rechargeable batteries are indicated in a wide range given the diversity of these systems \(^{[19]}\).

Batteries, like Li-Ion batteries for example, have a large success in embedded systems for portable electronics and for light-duty vehicles, whereas other kind of batteries like Lead-acid are more suited for heavy systems such as trucks or buses that require high storage capacity. Unlike batteries, which will not be treaded in this manuscript, supercapacitors, also known as electrochemical capacitors (ECs), can operate at high charge and discharge rates over an almost unlimited number of cycles. They display much higher power density in the order of kW/kg at the expense of a low energy density (1 - 10 Wh/Kg) \(^{[20]}\).
1.3 – Carbon-based materials

Carbon materials are abundant natural resources for the development of electrochemical energy storage devices. Carbon is an element that lends itself to our interest given the uniqueness of the electrical properties and different allotropic forms in which it occurs. Its sp² hybridization (with three σ electrons and one π electron) is of particular importance. Carbon atoms in sp² hybridization offer an unlimited number of nanostructural arrangements such as flakes, fibers, spherical particles and nanotubes showing variable electrical properties suitable for a large number of industrial applications [21,22].

These materials contain often substitutions with heteroatoms such as oxygen, nitrogen and hydrogen. These are mainly present as functional groups along the margins and surfaces of these nanostructures. Due to their electrical conductivity, chemical stability and nanostructures associated to large surface area carbon-based materials have been widely used in energy storage applications.

Many nanocomposites, which include carbon as a filler component, provide high mechanical resistance. They also have interesting electrical properties such as low electronic percolation threshold [23], electrostrictive and piezoresistive properties [24,25], high permittivity for capacitive electrodes [26,27], high electronic conduction for flexible electrodes [28,29] or conductive flowable electrodes [30-32], depending on the amount of filler.

The above materials are often made by liquid processing. In this view, the study of colloidal dispersion of carbon-based particles in liquid media is of significant importance, especially in water for environmental and economic reasons. A large part of recent work focuses on CNT suspensions [33-36] and graphene-based suspensions [37,38] but carbon black particles are also very promising materials because of their low cost [39].

Usually, the suspensions of carbon materials are investigated at rest, or dried to formulate electrodes as in battery applications. However, their flow behavior is critical when new technologies, which exploit these materials in dynamic conditions such as, redox batteries or electrochemical flow capacitors, are considered. For example, graphene-based materials are now playing a significant role in energy materials, where they act not only as conductive additives in electrode assemblies, but also for their specific anisotropic shape, which provides a new route to achieve dielectric flowable media.
On the other hand, also the study of the electric properties and percolation behavior of carbon black dispersions, as flowable electrode, is experiencing a strong interest for flow-assisted electrochemical energy storage (FAES) \(^{[40]}\).

Given the morphological multiplicity of this material, in this thesis only two of the carbon allotropic forms will be presented. In detail, graphene-based dispersions will be studied, such as graphene oxide liquid crystals, as a two-dimensional materials (2D), for the liquid with potentially variable and high dielectric permittivity and carbon black dispersions (3D), as conductive flowable electrodes for capacitive energy storage. In particular, the dielectric and electrical properties of these flowable dispersions will be studied under static and dynamic conditions. Specifically in this thesis, the effect of the flow-rate on the local orientation and reorganization of the particles and their relative dielectric and electrical behavior will be studied. More detailed characteristics of the carbon-based materials are presented in the Table 1.2.

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon onions</th>
<th>Carbon nanotubes</th>
<th>Graphene</th>
<th>Activated carbon</th>
<th>Carbide derived carbon</th>
<th>Templated carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensionality</td>
<td>0-D</td>
<td>1-D</td>
<td>2-D</td>
<td>3-D</td>
<td>3-D</td>
<td>3-D</td>
</tr>
<tr>
<td>Conductivity</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>Moderate</td>
<td>Low</td>
</tr>
<tr>
<td>Volumetric Capacitance</td>
<td>Low</td>
<td>Low</td>
<td>Moderate</td>
<td>High</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Cost</td>
<td>High</td>
<td>High</td>
<td>Moderate</td>
<td>Low</td>
<td>Moderate</td>
<td>High</td>
</tr>
</tbody>
</table>

Table 1.2 - Different Carbon structures used in electrical energy storage systems, with onion-like carbon (0 D), Carbon Nanotubes (1 D), Graphene (2 D), Activated Carbons (3 D), and Carbide-derived Carbons (3 D) \(^{[41]}\).

1.3.1 – Graphene-based materials

Among the different morphologies that carbon materials can show, Graphene represents the most valuable two-dimensional allotrope. Graphene consists of an atomic layer of carbon atoms with sp\(^2\) hybridization arranged in a hexagonal lattice, with delocalized \(\pi\) -electrons. Because of its large theoretical specific surface area (2.600 m\(^2\)g\(^{-1}\)), high carrier mobility (2.0·10\(^5\) cm\(^2\)V\(^{-1}\)s\(^{-1}\)), remarkable thermal conductivity (3–5 kW m\(^{-1}\)K\(^{-1}\)), and excellent optical transparency (97.3%), graphene has raised interest in industry and research \(^{[42]}\).
However, while the single layer form exhibits quantum electronic properties, multilayer structures behave as semi-metals only if they are regularly stacked, as in pristine graphite. Single layer dispersions are stable only at low concentrations, whereas more concentrated dispersions can contain up to five layers (Few Layers Graphene, FLG). The final properties are affected by the number of layers and their stacking reorganization.\[^{43}\]

Graphene-based materials, are usually produced by mechanical exfoliation of a highly oriented pyrolytic graphite (HOPG).\[^{44}\] Other methods include epitaxial growth onto SiC wafers, chemical vapor deposition (CVD),\[^{45}\] electric-arc discharge,\[^{46}\] or using a metal intercalated multi-layered graphene.\[^{47}\] Solution-based methods have been also developed using specific solvents, ionic liquids, and surfactant to disperse the particles. All these methods, however, are difficult to scale up for a massive, cheap and eco-friendly production. Moreover, graphene is insoluble in classical solvents and polymers.

On the other hand, Graphene Oxide (GO), the oxidized form of Graphene, is much easier to process in different solvents thanks to the presence of polar functional groups such as hydroxyl, epoxide and carboxylic groups, along the edges and on the basal plane of the flakes.\[^{48,49}\] The oxidation of Graphene can be achieved by following different procedures, such as Brodie,\[^{50}\] Staudnmaier,\[^{51}\] or Hummers methods.\[^{52}\]

Brodie and Staudenmair used a combination of potassium chlorate ($\text{KClO}_3$) in nitric acid ($\text{HNO}_3$), whereas Hummers method consists in treating graphite with potassium permanganate ($\text{KMnO}_3$) in sulfuric acid ($\text{H}_2\text{SO}_4$). However, the chemical oxidation of graphene significantly affects its conductivity due to local disturbances of the aromatic system within the basal planes, making it an insulator. The conductivity of graphene oxide needs to be eventually reactivated \textit{a posteriori} through different in-situ reduction processes.\[^{53}\]

Graphene oxide nanocomposites for energy storage have been extensively studied and some examples are reported in the next paragraphs. Until now, studies on these materials as flowable liquid crystals have only been focusing on their applications as electrorheological (ER)\[^{54}\] and magnetorheological (MR)\[^{55}\] fluids, but no work has ever suggested them as valid materials for energy storage applications.

The novelty of this thesis consists in proposing the implementation of smart dielectric fluids based on graphene oxide liquid crystals.
1.3.2 – Graphene Oxide materials in Electrochemical energy storage

Graphene oxide and its composites have been proposed as promising materials for different applications in energy storage and energy conversion. As a matter of fact, GO can be used as electrode for various lithium batteries or supercapacitors, or as dielectric material for dielectric capacitors.

Conventional electrodes for lithium-ion batteries (LIBs) have low theoretical capacity values. In this regard, elaborately designed GO-based composites exhibit superior electrochemical performances. For example, using GO combined with conductive graphite as anode increases the capacity of the system in average from values of 350 mAhg\(^{-1}\) to 650 mAhg\(^{-1}\) measured at 0.5 C\(^{\text{[56]}}\). In recent years there has been a strong interest in the development and optimization of Li-air batteries due to their high theoretical energy density. One of the main drawbacks of these batteries is that the diffusion path is blocked by discharged products (Li\(_2\)O\(_2\) and Li\(_2\)O). In this case, using cathodes made of GO materials allows a rapid oxygen diffusion due to the presence of defects and functional groups and increasing the capacity of the system\(^{[57]}\).

GO-based electrodes can be prepared by standard methodologies for film preparation, making sure that the preparation and functionalization procedure is simple and reliable. For instance, starting from a stable colloidal suspension of GO, different strategies can be adapted to control GO self-assembly and organization on electrode substrates (such as Au, glassy carbon, and quartz glass).

One of these methods involves the evaporation of a thin film of a GO suspension onto the desired supports at specific humidity conditions and temperature. It allows the control of wrinkles and patterns in the graphene oxide films during solvent evaporation\(^{[58]}\). Alternative approaches are the spin-coating procedure, which allows improvements of the final thickness and homogeneity of the film by controlling the process parameters (spinning speed, acceleration, and the number of spin-coating cycles, to name some) or the Langmuir-Blodgett (LB) technique that gives GO monolayers. Some other techniques involves the electrostatic interaction between the polar groups of GO flakes and a positively charged self-assembly monolayer (SAM), tailoring the structuration of the final films\(^{[59]}\).
Unfortunately, the poor electronic conductivity of GO has discouraged its use as active material in electrodes for supercapacitors, although there have been some investigations that demonstrated some feasibility \cite{60,61}.

In this case, a chemical reduction of GO is necessary to restore the $\pi$ character of the system and increase its conductivity. In general, the use of GO as electrode in supercapacitors is required when its electric double layer capacitance and pseudo-capacitive effects due to the interaction of the GO functionality with the electrolyte are needed \cite{62,63}. As reported in the literature, when it is used in combination with other conductive carbon materials, the capacitance of the system is greatly enhanced and the high surface area of the electrode improves the diffusion of the charged species within the material, by acting as a spacer for conductive materials \cite{64-66}.

Recently, several works have proposed GO, given its insulating behavior, as an excellent candidate for energy storage applications as a dielectric material, in composites and thin films and even in their dispersions \cite{67-73}.

According to the authors, the different degree of polar functionality present on the basal plane of these particles and along their edges would increase their electronic polarizability with the effect of presenting high dielectric constants of this material. Particular attention has been paid in this manuscript to this feature of GO. More details will be presented in the following chapters. In particular, we will evaluate the potential of GO as an additive for high permittivity materials, and discuss results reported until now in the literature.

### 1.4 – Carbon black dispersions in Electrochemical Energy Storage

Carbon black (CB) is a generic term to describe a heterogeneous mixture of carbon particles with a less graphitic structure. Fitzer \textit{et al.} defined CB as an industrially manufactured colloidal carbon material in the form of spheres, with fused aggregates smaller than 1000 nm \cite{74}. After these definitions, the concept of CB is commonly defined as a form of carbon with relatively high surface-area-to-volume ratio, produced by the incomplete combustion of fossil fuels. At different scales, it is possible to distinguish three different structural hierarchies in carbon black showed in Figure 1.2.

At small scales, we can identify the primary particles or permanently fused nodes with an average diameter of 30 nm. The nodules form aggregates of 50-500 nm in size.
These aggregates, in turn, form larger agglomerates (1-10 μm in size) through diffusion limited aggregation clusters (DLA) driven by short-range attractive interactions. This typical hierarchical structure makes carbon black different from all the other types of carbon-based conductive materials such as carbon nanotubes, carbon fibers, graphene sheets or graphite powder [75,76]. Because of its electrical and mechanical properties, carbon black is used in a wide range of industrial applications as an additive for composite materials [77], paints [78], conductive inks [79], rubbers [80] and in electrochemical energy storage system as active materials in solid electrode [81].

In the last decade, carbon black dispersions have been also used in different flow-assisted electrochemical energy storage systems (FAES), as flowable electrodes in semi-solid flow batteries (SSFB) [82] or as active materials in the electrochemical flow capacitor (EFC) [32] or in the flow capacitive deionization of water (CDI) [83].

Percolated CB slurry has a moderate viscosity that allows the flowing of the dispersion without clogging. These slurries can be used in FAES. In literature, several works proposed flowable CB dispersion as good candidates for flowable electrodes, but due to the difficulties in achieving a compromise between high conductivity and low viscosity, the electronic conductivities do not exceed 0.1 mS/cm in water or 1.7 mS/cm in oil to maintain a low viscosity [84-87].

In the above-mentioned applications, the CB dispersions must show specific electrical performances. As it is known, the electrical characteristics of these dispersions change...
dramatically around the percolation threshold \[^{[88]}\]. Given the morphological hierarchy of the CB, it is important to take into account how this morphological condition evolves during application of a mechanical stress. Below the percolation threshold, the CB dispersions show poor electrical performances but, at the same time, they have low viscosity, making them more suitable for applications where their flow is necessary. Even though they will not suffer from clogging effects, their flow would not guarantee the desired electrical performance.

At the percolation threshold, a 3D continuous network of carbon clusters will form, causing a sudden increase in viscosity and conductivity. Above percolation, very viscous conductive carbon dispersion, incapable of flowing, is obtained.

In this manuscript, special attention will be devoted to the use of flowable carbon dispersion for the capacitive energy storage and their specific use in the electrochemical flow capacitor to which a full chapter will be dedicated. Below will be reported some examples of technologies which exploit carbon back dispersions.

### 1.5 – Supercapacitors

A conventional capacitor is a system made of two conducting plates (the electrodes) separated by a dielectric material (Figure 1.3). When the electrodes are subjected to a potential difference, charges in the dielectric medium accumulate on the surface of the electrode with opposite sign.

This generates an electric field that can be exploited to store energy. Each capacitor is characterized by a parameter called capacitance \( C \), expressed in Farad and defined as the ratio of the electric charge \( Q \) on each electrode to the applied voltage \( V \).

For a conventional capacitor, the capacitance \( C \) is directly proportional to the dielectric constant of the dielectric medium \( \varepsilon_r \) and to the surface area \( A \) of each electrode, and inversely related to the distance \( d \) from each other:

\[
C = \frac{Q}{V} = \varepsilon_0 \varepsilon_r \frac{A}{d} \quad (1.1)
\]
Here, $\varepsilon_0$ is dielectric constant of the vacuum. The performance of a conventional capacitor is also described by its energy density (W/Kg) and power density (Wh/Kg).

![Schematic sketch of a conventional dielectric capacitor in a RC circuit.](image)

The energy density is the energy stored in the capacitor per unit volume and is directly proportional to its capacitance:

$$E = \frac{Q^2}{2C} = \frac{1}{2} QV = \frac{1}{2} CV^2 \quad (1.2)$$

The power density is the amount of power (time rate of energy transfer) per unit volume and it is a measure of how fast the discharge process is. The power density is related to the applied voltage and to the total resistance of the system, given by the contribution of all the components of the circuit (including the capacitor itself). The total resistance of the system is called equivalent series resistance (ESR) and it affects the discharge process of the stored energy, limiting the performance of the capacitor. The maximum power density that a given system can exhibit is expressed by the following expression (1.3):

23
Usually, conventional capacitors display high power densities, but relatively low energy densities when compared to other electrochemical storage devices, such as electrochemical batteries or fuel cells.

This means that batteries can store a higher amount of energy but they do not deliver it in a short time, because of their low density power. On the other hand, conventional capacitors store less energy per unit mass or volume, but their discharge process is fast, producing a high power.

In order to increase the performance of conventional capacitors and achieve power densities comparable to those of electrochemical batteries and fuel cells, supercapacitors, also known as electrochemical double-layer capacitors (EDLCs), have been developed.

Supercapacitors, showed in Figure 1.4, have polarizable electrodes made of porous carbon materials with a high surface area $A$, separated by an electrolyte between the electrodes.

The conversion and storage of electrical energy in supercapacitors occurs through the separation of ionic charges of the electrolyte on the surface of the electrodes and the formation of an electric double layer (EDL) at the interface between the electrode and the electrolyte, without involving any faradaic processes (red-ox) reactions.

The performance of supercapacitors is correlated to the ability to form the electric double layers (EDL), to the diffusion of electrical charges and to the morphology of the electrode surface. The mechanisms and the physics of electrochemical double-layers have been described in the past by using different models, which vary in accuracy and details. In the end of 19th century, Helmholtz proposed a first model of the double layer to describe the electrode/electrolytes interface.

However, this model did not consider important factors such as the diffusion of ions in solution or their possible adsorption onto the surface, and the interaction between solvent dipole moments and the electrode.

Successively, Gouy and Chapman in the beginning of last century improved this model by introducing diffuse model of the double layer, in which the concentration of charged species and the electric potential decrease as a function of the distance from the electrode.
Finally, in the 1924 Stern proposed a new model, which combines the other two, describing a formation of a dense layer of charges species adsorbed on the surface of the electrodes, and accounts for ions' finite size \(^\text{[89]}\).

Figure 1.5 - Schematic representation of electrical double layer structures according to (a) the Helmholtz model, (b) the Gouy-Chapman model, and (c) the Gouy-Chapman-Stern model.
1.5 - **Electrochemical Flow Capacitors (EFC)**

The electrochemical flow capacitor (EFC) is a new technology, developed at Drexel University, by Yuri Gogosti team for grid-scale capacitive energy storage. This new technology benefits from the advantages of both supercapacitors and flow batteries. In detail, it exploits the fast combination of charge/discharge process and the long cycle lifetime of supercapacitors. It enables in principle energy storage and power to be decoupled and optimized for the desired application through the specific design of size of the system as in the flow battery \[^{[31]}\].

The novelty of this technique consists in the use of a flowable carbon-based dispersion (slurry) as flowable electrodes for capacitive energy storage. The exploitation of aqueous carbon dispersion limits the system in term of energy density, when compared with classical rechargeable batteries. This is due to the limited stability of an aqueous electrolyte to the operation voltage of the systems. Due to these limitations, several studies are focused in the optimization of the electrical performance of the active material throughout different strategies such as the exploitation of pseudocapacitive processes to enhance the capacitance of the system, or using organic electrolytes to enlarge the applied voltage windows \[^{[90]}\]. The operating principle of an EFC is reminiscent of that of flow batteries. Specifically, the electrochemical cell consists of two compartments separated by an electrically insulating membrane, which is selective only to the electrolyte's ions in which the active material is dispersed.

These two compartments are in contact with the current collectors and are the channel where the flowable carbon electrode acts as anode and cathode. These channels are in turn, connected to respective two vessels that host the charged and uncharged slurry. During the charging process, the slurry is transferred by means of pumps from the vessel in which it is uncharged to the electrochemical cell in which, through the application of an electric field, it is loaded. The charging process provides the charge balance by the diffusion of the electrolyte ions through the membrane. Once the slurry is loaded, it is transferred to the other two vessels in which it is stored. In every vessel, the total charge is close to zero as the electric charge on the active material is balanced by ions of the opposite charge.

By contrast to traditional capacitors, in which the active materials represent in average 90 % of the total mass, in flowable electrodes the majority of the material is given by the
electrolyte in which carbon is dispersed. Moreover, in the former the active material is constantly in contact with the electroactive area while in flow-assisted electrochemical system the active material flows into and out of the electroactive area. These specific differences do not allow a simple comparison of the performances between the two systems.

![Diagram of an electrochemical flow capacitor](image)

*Figure 1.6 – Schematic of an electrochemical flow capacitor*

Nevertheless, the challenge in the field consists in developing new fluids with low viscosity and high conductivity and capacitance. The combination of these properties is not straightforward, and calls today for more research. Systems shown until now are still unsuitable for applications considering their insufficient electrical conductivity and high viscosity. The high viscosity is associated with a large loss of energy needed to flow the active fluid. The development of new fluids with improved properties is an important motivation of work presented further in this thesis.
Chapter I

Carbon-based materials for energy storage

Reference


Chapter I

Carbon-based materials for energy storage


[64] Lin, L.-Y.; Yeh, M.-H.; Tsai, J.-T.; Huang, Y.-H.; Sun, C.-L.; Ho, K.-C. A Novel Core–Shell Multi-Walled Carbon Nanotube@Graphene Oxide Nanoribbon Heterostructure as a Potential Supercapacitor Material. J. Mater. Chem. A 2013, 1, 11237–11245


Chapter II

Materials and Methods
2.1 – Introduction

The main challenge of the thesis is to develop carbon-based liquid media for both mechanical energy harvesting, sensing or capacitive energy storage. The implementation of these liquid media envisages the screening of different formulation protocols, such as the choice of surfactants, dispersion and centrifugation processes in order to guarantee the desired rheological and electrical properties. In addition it is crucial to fully understand the electrical, dielectric and rheological properties of the materials. Consequently, we developed specific characterization techniques and experimental setups to study these properties under the static and dynamic conditions.

This chapter is described as follows. In the first section, we describe the materials and methods that were used in order to prepare the carbon-based dispersions. The second is devoted to the characterization techniques enabling the determination of the dielectric and electrical properties of these materials.

2.2 – Materials for flowable carbon-based dispersions

Commercial GO solutions in water with a concentration of 4 mg/ml were purchased from Graphenea. These dispersions are prepared by chemically processing raw graphite material in water via the modified Hummers method \(^1\). The monolayer content (measured with 0.05 wt% dispersion) reaches values up to 95% and the single layer has a sheet dimension of 5-7 μm. We used Milli-Q water with a resistivity above 18.2 MΩ·cm at 25 °C. 2-Propanol (IPA) absolute 99.9% were purchased from Sigma Aldrich and used as received.

Ketjenblack EC 600JD and compressed carbon Acetylene black powders were purchased from AkzoNobel and Alfa Aesar. Carbon suspensions are prepared as follows. Firstly, 1.5 wt% of arabic gum (Molekula, CAS Number 9000-01-5) and 0.5 wt% of sodium alginate (Aldrich, CAS Number 9005-38-3) are dispersed in a solution of ammonium sulfate, \((\text{NH}_4)_2\text{SO}_4\) 2 M (Aldrich, CAS Number 7783-20-2). This dispersion represents the continuous phase of the carbon black dispersion. Once it has been achieved, the desired amount of carbon powders is dispersed with a particular protocol shown in the following paragraphs.
2.2.1 – GO sample preparation

The GO dispersions in Milli-Q water or isopropyl alcohol (IPA) were obtained through a solvent exchange process. Firstly, the commercial dispersion was sonicated by using tip sonication at 135 Watts for 30 min (Branson Sonifier 450A) to unbundle GO aggregates and homogeneously disperse the flakes. Subsequently a gentle centrifugation (Jouan B4i Multifunction, rotor S40) at 1400g was performed for 20 minutes in order to precipitate the large-sized aggregates that were not separated in previous processes. From the resulting dispersion, 95 mL of supernatant is withdrawn for further centrifugation process (Sorval RC 6+, rotor SE-12) at 50000g for 1h. Figure 2.1 shows the overall processes for the exchange of solvent in IPA but the same protocol was applied for the preparation of GO solution in Milli-Q water. To avoid confusion we only present the process in IPA in Figure 2.1.

Figure 2.1 – (A) Detailed sequence of sonication and ultracentrifugation processes to obtain high-concentration GO. (B) Schematic sequence of the exchange of solvents method.
The collected slurry was then dissolved in pure IPA and the obtained diluted dispersions were then centrifuged at 1400 G for 20 minutes in order to precipitate any large aggregates. As previously mentioned, the supernatant was collected and we applied the same procedures to perform the second and third solvent exchange. Afterwards, the achieved GO/IPA dispersion was sonicated with a tip Branson Sonifier 450A for 30 minutes at 135 W to further improve the dispersion state of GO flakes. This procedure allows the unbundling of the small aggregates. The obtained dispersions were then subjected to a final ultracentrifuge process at 50000 G for 1 hour to achieve GO gel with a high concentration of 55 mg/mL. Samples with different weight percentage (wt%) of GO flakes were prepared by dilution in IPA. The GO dispersions in Milli-Q water were prepared with exactly the same protocols.

2.2.2 – Carbon black sample preparation

Carbon black dispersions are prepared by mixing them with a water solution, which consists of 1.5 wt% Arabic Gum, 0.5 wt% Sodium Alginate, and 2M ammonium sulfate. In this dispersion, the Arabic Gum acts as a highly effective non-ionic surfactant for the dispersion of carbon particles whereas polyelectrolyte, Sodium Alginate, has been chosen to serve as stabilizer for the carbon dispersion as it avoids the sedimentation process of the carbon particles and ensures a constant conductivity over time. The solution was heated for 1 h at 80 °C under magnetic stirring until complete dissolution of polymers [2]. Subsequently, we proceed the grinding of the carbon powder with the aid of a mortar in order to obtain a fine control of the size of particles. This procedure facilitates the wettability process of the carbon particles and consequently their dispersibility. After cooling, carbon black particles are added with the desired proportions and the blend is kept under stirring for several minutes until the carbon black is totally wetted by the aqueous solution.

Finally, to homogenize the dispersion, mechanical shear stress was applied with a high shear mixer (Silverston L4RT) for 30 min at a given rotation speed of 5000 rpm, with corresponds to an applied shear rate of 3500 s⁻¹. Below, Figure 2.2 shows a graphic scheme of the process to prepare the flowable carbon electrodes.
2.3 – Polarizing optical microscopy

Polarizing optical microscopy of GO dispersions in Milli-Q water and isopropyl alcohol are shown in Figure 2.3. Samples were studied between glass slides with a Leica DM 2500 P polarizing microscope at resolution 2592×1044 pixels at room temperature. GO flakes are homogeneously dissolved at low concentration (below 0.4 wt%), with a small number of microscopic aggregates. Cross-polarizing pictures showed increasing birefringence (light spots) approaching the biphasic-nematic phase boundary (around 0.8 wt% GO) for both solvents. In the nematic phase (Figure 2.3 (D-E),(I-J)), no clear aggregation is detected. The flakes alignment is increasing, as evidenced by the increasing size of birefringent domains. Due to the large size distribution, no clear lamellar phase is observed, as expected for monodisperse plate-like nanoparticles systems. Figure 2.4 shows optical micrographs of Ketjenblack dispersions in Arabic gum 1.5 wt% Sodium alginate 0.5 wt% in (NH₄)₂SO₄ 2M in the investigated concentration range. Carbon black dispersions were studied in the same condition aforementioned. Ketjenblack powders form large aggregates with uneven sizes around 10 µm. The increase in CB loading enlarges the agglomerates and, progressively a conducting network pathway is constructed.
Figure 2.3 – Optical micrographs of GO dispersion in milliQ water and isopropyl alcohol. (A,A’) 0.4 wt%, (B,B’) 0.6 wt%, (C,C’) 1.0 wt%, (D,D’) 1.5 wt%, (E,E’) 3.0 wt% in milliQ water. (F-F’) 0.4 wt% (G,G’) 0.6 wt%, (H,H’) 1.0 wt%, (I,I’) 1.5 wt%, (J,J’) 3.0 wt% in Isopropyl alcohol. The axes of the crossed polarizers are in horizontal and vertical directions. The observed textures reflect the formation of small monodomains of nematic LC phase. (Scale bar 200 µm).

Figure 2.4 – Optical micrographs of Ketjenblack dispersion in Arabic Gum 1.5 wt% - Sodium Alginate 0.5 wt% in (NH₄)₂SO₄ 2 M. (A) 2.0 wt%, (B) 3.0 wt%, (C) 4.0 wt%, (D) 5.0 wt% (E) 6.0 wt%, (F) 7.0 wt%, (G) 8.0 wt%, (H) 9.0 wt% (Scale bar 50 µm).
2.4 – Dielectric measurements

The dielectric properties of the obtained dispersions were studied by using an impedance analyzer (7260 Impedance Analyzer, MaterialsMates Italy) under a voltage of 50 mV in a frequency range of $10^1 – 10^6$ Hz. The measurements were performed using a home-built dielectric measuring cell made of Polyether ether ketone (PEEK) with Platinum blocking electrodes with surface areas of 96 mm$^2$, resistance of 0.2 Ω and thickness of 690 µm. The cell thickness was calibrated by means of a reference solvent (NaCl 1mM).

![Image of dielectric cell](image)

Figure 2.5 - The schematic image of the home-made dielectric cell used in this thesis. The inlet and outlet present on top of the dielectric cell are necessary to insertion of the sample and for the connection with the syringe-pump for the flow dependent dielectric measurements.

We stress that the large surface area of the electrodes and the thin thickness were chosen to maximize the contribution of the bulk relative to the polarization of the electrodes. Indeed, in a number of previous works, it appears that determination of the dielectric constant of liquids can be challenging when charged species adsorb at the surface of the electrodes $^{[3]}$. The charged species create a double layer which acts as an effective capacitor with a very high capacitance. The contribution of this effect is often referred to as “electrode polarization”. It is critical to have a bulk capacitance (sometimes called geometric capacitance in the literature) as large as possible to enable the reliable determination of the dielectric constant of the bulk, besides the electrode polarization effect. A number of indirect methods have been proposed in the literature to correct data and remove indirectly the contribution of the polarization of the electrodes $^{[4]}$. 
But these methods are poorly satisfactory, and as shown further, we decide in this thesis to correct the data just to remove the contribution of cables and sample-holder to the measured impedance. After a number of unsuccessful trials, we decided to not attempt to remove the contribution of the polarization of the electrodes. Instead, we will include this contribution in the modeling of the systems. Because, the capacitance of the bulk is enhanced by the specific geometry of our cell, we will see in chapter IV, that this approach allows a fitting of the data with a clear distinction of the contribution of the bulk and of the electrodes. This is why our approach allows a reliable determination of the permittivity of the carbon based fluids investigated in this thesis.

Our correction procedure involves just correcting the measured impedance values by removing from them the resistive contributions due to the coaxial cables and the sample-holder. This method consists in measuring three values of impedance: a resistive contribution obtained through a short circuit of the system, a capacitive contribution, obtained by an open circuit measurement and the impedance measurement of the sample. Figure 2.6 shows the RC equivalent circuit of the three contributions. Below the mathematical treatment is reported.

\[
\frac{1}{C_0} = \frac{1}{C_1^+} + \frac{1}{C_2^-}
\]

Figure 2.6 – Equivalent circuit of the three electric contributions for the correction method.
• **$Z_1^*$ - Short Circuit**

\[ Z_1^* = Z_{RC}^* \] (2.1)

• **$Z_2^*$ - Open Circuit**

\[ Z_2^* = Z_{c0}^* + Z_{RC}^* \] (2.2)

with:

\[ \frac{1}{C_0} = \frac{1}{C_1^*} + \frac{1}{C_2^-} \] (2.3)

Where, $C_1^+$ and $C_2^-$ represent the capacitance of the two coaxial cables.

• **$Z_3^*$ – Sample**

\[ Z_3^* = Z_{RC}^* + \frac{1}{Z_s^* + \frac{1}{Z_{CO}}} \] (2.4)

and defining the admittance $Y_s^*$ as the reciprocal of the impedance, we obtain:

\[ Y_s^* = \frac{1}{Z_s^*} = \frac{1}{Z_3^* + Z_{RC}^*} - \frac{1}{Z_2^* + Z_{RC}^*} \] (2.5)

Therefore the impedance measurement of the studied sample will be a function of both contributions: a purely resistive one, $Z_1^*$ and purely capacitive $Z_2^*$.

\[ Z_s^* = f(Z_1^*, Z_2^*) \]

The impedance correction procedure was performed for all measurements made in this manuscript. Flow dependent dielectric measurements have been performed by means of connecting the dielectric cell to a syringe-pump which allows the flow of the dispersion.
inside the dielectric cell at different flow rates. The experimental set-up used for these measurements is shown in Figure 2.7.

![Figure 2.7 - Flow dependent AC dielectric measurements set up.](image)

**2.5 – AC electrical measurements under shear**

The AC electrical impedance measurements under shear were performed, in the same condition aforementioned, by using a rotameter (Caplim Rheophysique West 3400) connected to the impedancemeter as shown in Figure 2.8. This experimental set-up enables the analysis of the dynamic properties of the sample in a wide range of shear rate up to 1200 sec⁻¹.

This apparatus consists of a specific cylindric sample-holder in Polyether ether ketone (PEEK) using blocking circular gold electrodes with surface areas of 770 mm², resistance of 0.3 Ω and thickness 0.6 mm. In order to obtain the apparent shear rate values from the rotameter revolutions, a conversion protocol was carried out. In order to obtain the apparent shear rate values from the rotameter revolutions, a conversion protocol was carried out.
In order to obtain the apparent shear rate values from the rotameter revolutions, a conversion protocol was carried out. Successively it is measured the rotameter speed of revolutions $\omega$, in rad/sec which allow the apparent shear rate $\dot{\gamma}$ to be obtained through the Moon-Ewart coefficient.

$$F_\gamma = \frac{R_2^2 + R_1^2}{R_2^2 - R_1^2}$$

$$\dot{\gamma} \ [sec^{-1}] = F_\gamma \omega$$

Figure 2.9 – Schematic representation of the sample-holder geometry in AC electrical measurement under shear ($R_1 = 0.01691 \ m, R_2 = 0.01751 \ m$ and $F_\gamma = 28.692049$).
Table 2.1 – Table of conversion values at different shear rates

<table>
<thead>
<tr>
<th>Sec per cycle</th>
<th>rps</th>
<th>rpm</th>
<th>$\omega$ [rad/sec]</th>
<th>Shear rate $\dot{\gamma}$ [sec$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2786</td>
<td>0.3050</td>
<td>18.3050</td>
<td>1.9169</td>
<td>55</td>
</tr>
<tr>
<td>1.8031</td>
<td>0.5546</td>
<td>33.2812</td>
<td>3.4852</td>
<td>100</td>
</tr>
<tr>
<td>1.0016</td>
<td>0.9984</td>
<td>59.9070</td>
<td>6.2735</td>
<td>180</td>
</tr>
<tr>
<td>0.7211</td>
<td>1.3867</td>
<td>83.2049</td>
<td>8.7132</td>
<td>250</td>
</tr>
<tr>
<td>0.5633</td>
<td>1.7750</td>
<td>106.5023</td>
<td>11.1529</td>
<td>320</td>
</tr>
<tr>
<td>0.4507</td>
<td>2.2187</td>
<td>133.1276</td>
<td>13.9411</td>
<td>400</td>
</tr>
<tr>
<td>0.3679</td>
<td>2.7180</td>
<td>163.0819</td>
<td>17.0779</td>
<td>490</td>
</tr>
<tr>
<td>0.3402</td>
<td>2.9391</td>
<td>176.3946</td>
<td>18.4720</td>
<td>530</td>
</tr>
<tr>
<td>0.3005</td>
<td>3.3269</td>
<td>199.6770</td>
<td>20.9117</td>
<td>600</td>
</tr>
<tr>
<td>0.2403</td>
<td>4.1602</td>
<td>422.6147</td>
<td>26.1396</td>
<td>750</td>
</tr>
<tr>
<td>0.1952</td>
<td>5.1032</td>
<td>306.1943</td>
<td>32.0646</td>
<td>920</td>
</tr>
<tr>
<td>0.1832</td>
<td>5.4569</td>
<td>332.8197</td>
<td>34.8528</td>
<td>100</td>
</tr>
</tbody>
</table>

2.6 – Rheology measurements

To measure the viscosity and the shear stress as a function of the shear rate, an AR1000 controlled stress rheometer from TA instrument is used. The geometry used is a Plessy glass plate of 60 mm in diameter and with a gap of 800 µm relative to the bottom plate.

Several tests, which are not reported in this manuscript, were conducted on the choice of the gap demonstrate that the results are independent on its width for gaps larger than 500
µm. A ramp of shear rate is applied from 500 s\(^{-1}\) to 0.1 s\(^{-1}\), with 10 points per decade. Each shear rate is maintained during 30 sec and the viscosity is measured by averaging the measurements over the last 5 sec. The temperature is set with a Peltier system at 20° C.

### 2.6 – Flow assisted Charge and Discharge

Flow assisted charge and discharge processes of a carbon liquid electrode was performed by using a wave-form generator (Trueform 33500B, Keysight) connected to a RC circuit at 1 V for 200 seconds by using a resistance of 178 Ω. In this phase, the uncharged carbon dispersion is pumped through syringe-pumps through the electrochemical cell, where the electric field charges the carbon dispersions in opposite sign.

![Diagram](image)

**Figure 2.11** – Scheme of charge and discharge processes in electrochemical flow capacitors.

The voltage applied to the RC circuit and across the electrochemical cell was recorded by means of an oscilloscope (Tektronix DPO 2022B) by using two different channels, as shown in Figure 2.12 (A).
Figure 2.12 – Experimental set-up for flow assisted Charge and Discharge (A). Geometry and materials used in the electrochemical two-compartment cell. (B) Geometry and materials used in the electrochemical two-compartment cell.

The charged slurries are collected in the other two syringes, which act as vessels and where the carbon dispersion is stored. During the discharge process the circuit is short-circuited by means of a switch. This procedure allows us to perform voltage measurements related only to the decoupling of the electric double layer without other influences. More detailed features of the electrochemical two-compartment cell are shown in Figure 2.12 (B).
Reference


Chapter III

Electrostrictive soft materials for sensing and mechanical energy harvesting
3.1 – Introduction

In the last years, the demand for new technologies for energy conversion is dramatically increasing to satisfy the various needs in portable electronics, or just to power wireless micro-systems or simple autonomous sensor networks, etc. Harvesting energy from ambient mechanical vibrations is one of the most promising approaches to power wireless micro-electro-mechanical systems (MEMS) and low power devices \cite{1-6}. Sources of ambient mechanical vibrations, as shown in Figure 3.1, are abundant and of different nature. We can distinguish two classes of vibration according to their intensity: “high” level vibrations correspond to large industrial equipment, transports, continuous or natural movements such as ocean waves; “low” level vibrations include human motions, such as running, movements of structures such as doors, panels, walls or floors. All these different types of vibrations potentially could provide enough energy to satisfy power demands of autonomous electronic systems \cite{7-11}.

![Figure 3.1- Power densities of ambient mechanical energy sources.\cite{4}](image)

Electrostrictive materials exhibit changes of dielectric properties when they are deformed \cite{12-13}. When used in variable capacitors, they present several advantages compared to other mechanical energy harvesters, such as piezoelectric or electromagnetic systems. In particular, they can be used in many devices since they cover the widest range of frequencies of operation \cite{14-16}.

An interesting approach to make electrostrictive materials presented in several works in literature is based on the incorporation of polymer nanocomposites with conductive nanoparticles that increase the dielectric constant of the material \cite{17-18}.
Non-percolated nano-carbon based polymer nanocomposites can exhibit large changes of capacitance in response to a mechanical deformation \cite{19}. Nevertheless, this technology is still far from being optimized for applications because the permittivity of these materials is not yet sufficiently large and the stress responsiveness, and then the variations of capacitance, remains limited.

![Comparison among the operation frequency ranges for transducers based on different functioning mechanisms: Electrostrictive, Magnetostrictive and Piezoelectric.](image)

As carbon-based nanocomposites, even heterogeneous fluids formed by highly polarizable particles, such as Graphene Oxide (GO), should display a high dielectric constant. GO is considered a promising component for electronics because of its unique anisotropy, easy processing and potential giant permittivity \cite{20,22}. The latter would arise from an enhanced electronic polarizability due to the presence of functional groups at the surface and at the edges of GO particles \cite{23}. As a matter of fact, several publications have reported a very large permittivity of GO materials \cite{24,26}. In this work, we will explore the potential use of GO as electrostrictive soft material for mechanical energy harvesting and therefore for the implementation of smart materials that alter their dielectric properties in response to a mechanical stimulus. This work clarifies if the use of GO is a promising way to design new high dielectric fluid whose properties are sensitive to the flow and provides insights into the mechanism of variation of capacitance in electrically heterogeneous systems. Being fluid, they could also be particularly useful as ultrasensitive pressure sensors, a field of growing interest in particular for medical applications (artificial skin, blood pressure, heart rate, etc) \cite{27,28}.
3.2 – Variable Capacitors

Electrostatic transduction, which uses variable capacitors, is one of the different methods for converting electrical energy from vibrations. In these transducers, the mechanical vibration causes capacity variations, which can then be converted into electrical energy with a conditioning circuit. These capacitors consist of two metallic plates electrically separated by a dielectric material. When a potential \( U \) is applied between the two plates, they acquire a charge \( Q \) of opposite sign, related to the capacitance \( C \), as follows:

\[
C = \frac{Q}{U} = \varepsilon_0 \varepsilon_r \frac{A}{d}
\]  

(3.1)

Here \( A \) is the surface of the plates, \( d \) the distance between them, \( \varepsilon_r \) the dielectric permittivity of the medium and \( \varepsilon_0 \) the dielectric permittivity of the vacuum. The energy stored in the capacitor is expressed by the equation:

\[
E = \frac{1}{2}QU = \frac{1}{2}CU^2 = \frac{1}{2} \frac{Q^2}{C}
\]  

(3.2)

By contrast to piezoelectric and electromagnetic devices, the conversion mechanism of electrostatic transducers requires an external voltage to start the process. The resulting variations of capacitance can be translated into electrical energy in different ways, for instance, by using cycles. Commonly, cycles are performed at constant charge or constant voltage. In practice, more complex cycles can be realized to achieve better efficiency. Nevertheless, model cycles are still useful to show and discuss principles of energy conversion in variable capacitors.

Figure 3.3 shows the charge constrained cycle of a variable capacitor. Before the cycle starts, the variable capacitor is electrically neutral and its charge is \( Q_0 = 0 \) (Figure 3.3 (a) and (b)). When the system is plugged to an external source of voltage, the cycle starts and the induced polarization produces a constant charge equal to \( Q_{\text{cst}} \).
In this initial state, the variable capacitor has a maximum capacitance $C_{\text{max}}$. At a given voltage $U_{\text{min}}$, the capacitor is able to store a specific charge. When the external source of energy is switched off, an open circuit at a charge $Q_{\text{cst}}$ is created. At this stage, a mechanical work is provided in order to change the capacitance from $C_{\text{max}}$ to $C_{\text{min}}$ at constant charge. As a consequence, the voltage across the variable capacitor increases to $U_{\text{max}}$.

Figure 3.3 – (a) Scheme of the energy conversion cycle at constrained charge of a variable capacitor. The dark-grey rectangle represents the fixed electrode whilst the light-grey one represents the mobile electrode. (b) Standard energy conversion cycle at constrained charge, the black arrows show the direction of the cycle.

Lastly, the capacitor is discharged and the gained electrical energy during the process can be collected or used in a resistive device. The energy output per cycle is expressed by the equation (3.3).
\[ E = \frac{1}{2} Q^2_{\text{est}} \left( \frac{1}{C_{\text{min}}} - \frac{1}{C_{\text{max}}} \right) = \frac{1}{2} U_{\text{max}} U_{\text{min}} (C_{\text{max}} - C_{\text{min}}) \tag{3.3} \]

This equation shows that the variation of capacitance has to be increased as much as possible for efficient energy harvesting.

### 3.3 – Dielectric Relaxation

Colloidal suspensions of electrically charged flakes, such as GO, are widely used in liquid crystalline phases \([29,31]\). These systems are characterized by a high fluidity combined with a specific structural order that gives directional and anisotropic properties common to crystalline systems \([32]\).

In general, colloidal suspensions of geometrically anisotropic particles can form liquid-crystalline phases above a critical concentration, as shown in Figure 3.4. Above 1.0 wt% GO flakes spontaneously orient parallel to each other giving rise to a nematic phase. Below that concentration, a biphasic system is observed with nematic domains in equilibrium with the isotropic phase. Due to the large size distribution the phase boundaries are not well defined. Note that the nematic phases of GO are considered sometimes as pseudo-lamellar phases because the spacing between flakes is uniform \([33]\).

![Figure 3.4 – Arrangement of discotic particles in the Isotropic, Biphasic and Nematic liquid crystal phases.](image)
In this case, the system can be modelled as a heterogeneous medium composed of stacked dielectric insulating GO layers of thickness $\delta$ and complex conductivity $\sigma_p^*$ expressed as follow:

$$\sigma_p^* = 2\pi j \nu \varepsilon_0 \varepsilon_p$$

(3.4)

The layers of the dielectric materials are separated by a solvent layer of thickness $t$ and complex conductivity $\sigma_s^*$ given by the expression (3.5),

$$\sigma_s^* = \sigma_s + 2\pi j \nu \varepsilon_0 \varepsilon_s$$

(3.5)

where $\varepsilon_0$ is the permittivity of vacuum, $\varepsilon_p$ and $\varepsilon_s$ the dielectric constants of GO and of the solvent, $\sigma_s$ the conductivity of the solvent and $\nu$ the frequency.

Figure 3.5 – Schematic sketch of a pseudo lamellar phase made of platelet particles with respective thickness $\delta$ separated from each other by a layer of solvent of thickness $t$. On the right the Debye-type relaxation mode is proposed for a two-planar layer system, whose longitudinal direction is perpendicular to the vector of the electric field.
In this case, we can consider that $t\gg\delta$ and that the normal of the layers is parallel to the electric field. This specific arrangement of the flakes in a given media, shows a complex permittivity $\varepsilon_{eff}^*$ with a specific relaxation time $\tau_0 = 1/2\pi \nu_0$ given by the Debye-type relaxation:

$$\varepsilon_{eff}^* = \frac{\Delta \varepsilon}{1 + j\frac{\nu}{\nu_0}} + \varepsilon_s$$

(3.6)

where the amplitude $\Delta \varepsilon$ is related to the dielectric constant of the particle of GO as follow:

$$\Delta \varepsilon = \varepsilon_p \frac{t}{\delta}$$

(3.7)

and $\nu_0$, the characteristic frequency of the relaxation given by:

$$\nu_0 = \frac{\delta \sigma_s}{2\pi \varepsilon_0 \varepsilon_p}$$

(3.8)

The above expressions are derived further. The inclusion of GO in a given fluid is therefore expected to generate a dielectric relaxation with an amplitude that is proportional to its intrinsic value of dielectric constant. This is why very large relaxation amplitudes should reflect a giant dielectric constant of GO.

It is important to note that for other orientations of the particles, other amplitudes are expected. These variations in the amplitude, suggest a new approach to achieve changes of capacitances. This is why such materials could be potentially useful for new technologies of energy harvesting or pressure sensors. For example in perpendicular alignment, and at low volume fraction, we expect only negligible effects on the permittivity.

More details of these amplitudes of relaxation will be presented in the following paragraph.
3.4 – Electrostrictive soft materials

Smart materials are substances that can respond precisely to external stimuli, including temperature, pH alteration, photon irradiation, electric/magnetic field or mechanical stress \[^{[34]}\]. Electrorheological (ER) and magnetorheological (MR) fluids are known to be a type of the most significant stimuli responsive smart materials. These systems are in general made of electrically polarizable or magnetic particles dispersed in insulating media, which can be controlled by an external electric field or magnetic field respectively.

The effects of the electric field and the magnetic field generate structural changes of the particles, transforming the system from liquid-like to solid-like in a reversible switching \[^{[35]}\]. By contrast, to the latter, in which the structural changes are originated by the application of an electrical or magnetic field, we explore in this work an innovative approach to achieve a smart fluid sensitive to a mechanical stress. The application of this external input, such as mechanical vibration, human motion, variable pressure or flow of a solvent, can alter the structures of such systems with the consequent effect to change its dielectric properties (electrostriction effect).

A liquid crystal made of discotic particles can be considered as a system in which the structure can be sensitive to the application of mechanical stress.

Figure 3.6 – (A) Polarizing optical microscopy (POM) of a GO dispersion in Milli-Q water 0.4 wt% (Biphasic Phase) in a macrofluidic channel which reflects the geometry of the dielectric cell. The dark area in the channel suggests a planar alignment of the flakes parallel the cell walls and with the director $n$ of LCs domains parallel aligned to the polarized light beam. (Scale bar 2500 µm) (B) Scheme of the home-built macrofluidic device used for optical analysis.
In detail, a liquid crystal under dynamic conditions, e.i. flow conditions, could present a different structural arrangement from the one presented in static conditions. As previously indicated, the amplitude of relaxation $\Delta \varepsilon$ is closely related both to the intrinsic dielectric constant of the particle and to the structural arrangement of the flakes. The expression (3.7) is valid for insulating particles stacked in a pseudo-lamellar phase whose longitudinal direction is perpendicular to the electric field. The arrangement of our systems in this particular structure has been confirmed by polarizing optical microscopy, using a specific home-built macrofluidic device with exactly the same size of the dielectric cell, which was used to monitor the birefringence of the samples in static and dynamic conditions.

Figure 3.6 (a) shows a polarized light photograph of a GO dispersion 0.4 wt% in Milli-Q water under static conditions. Here, we can observe the dark area of the channel due to the alignment of the director of the GO flakes domains with the vector of the polarized beam, confirming what previously stated $^{[36]}$. The system remains dark when rotated with respect to the direction of the polarizers.

If the flow alters the local structure of the GO flakes in these dispersions, we should be able to detect changes in the amplitude of dielectric relaxation. It was reported that at high shear rates the spacing between the particles is reduced, as result of the shear-induced flattening of the GO flakes $^{[33]}$. As previously mentioned, the maximum amplitude of the dielectric relaxation is given when the normal of the GO layers is parallel to the electric field. By contrast, the minimum amplitude is given for a structural arrangement in which the normal to the flakes is perpendicular to the electric field. All intermediate conditions provide amplitude of dielectric relaxation within these two extreme limits. The effect of the solvent flow should alter the local orientation of the flakes and therefore it is plausible to expect that the flow can tune the dielectric properties of the material.

In this chapter, we will therefore evaluate the dielectric properties of GO dispersions in different polar solvents, in static and dynamic conditions in order to verify a potential variation of permittivity in dynamic conditions and therefore the ability to work as an electrostrictive fluid.
3.5 – RC Model

As previously mentioned, GO dispersions given the geometrically confined thickness of the dielectric cell, give a rise to a specific arrangement of the particles that we can consider as a pseudo lamellar phase made of stacked GO layers separated by solvent layers with a specific dielectric relaxation.

In order to describe the complex permittivity of this system, in both configurations, with the normal of the flakes oriented parallel and perpendicular to the direction of the electric field it is more convenient to analyze the associated RC circuit. The principle consists in using an elementary cell that represents the behavior of the all system considering the continuity of electric current and voltage throughout the medium. The GO flake is modeled as a circuit element with a resistance $R_p$ and a capacitance $C_p$ in parallel. The same holds for the solvent layers with $R_s$ and $C_s$. These circuit components are assembled in series to form a cubic elementary cell as shown in Figure 3.7.

![Figure 3.7](image)

**Figure 3.7** – (a) Schematic sketch of a cubic cell consisting of an insulating GO flake in the solvent with the direction of its normal parallel to the electric field. (b) RC model associated in terms of $R_s$, $C_s$, $R_p$ and $C_p$. (c) Resistance and capacitance of the particles and solvent expressed in terms of $t$ and $\delta$ for system in which the normal of the particles is parallel to the direction of the electric field.
As previously mentioned, we assume that the wall thickness is $\delta$ and specific complex conductivity $\sigma_p^* = 2\pi j \nu \varepsilon_0 \varepsilon_p$, and the distance between them is $t$ and specific complex conductivity $\sigma_s^* = \sigma_s + 2\pi j \nu \varepsilon_0 \varepsilon_s$.

The complex capacitance of this system showed in Figure 3.7 (a) can be expressed starting from the complex impedance expressed through the respective value of resistance and capacitance of their constituent members $^{[37]}$. In detail, the complex impedance of the system is given by the equation (3.10).

\[
Z^* (\nu) = \frac{2R_s}{1 + 2\pi j \nu R_s C_s} + \frac{R_p}{1 + 2\pi j \nu R_p C_p}
\] (3.10)

Starting from this impedance it is possible to calculate the capacitance of the system as a function of the frequency through the following expression:

\[
C(\nu) = \frac{Im(Z^{-1})}{2\pi \nu}
\] (3.11)

This capacitance can be expressed in the form of Debye type relaxation:

\[
C(\nu) = \frac{\Delta C}{1 + \left(\frac{\nu}{\nu_0}\right)^2} + C_\infty
\] (3.12)

where the $\Delta C$ is equal to:

\[
\Delta C = \frac{2R_s^2 C_s + R_p^2 C_p}{(2R_s + R_p)^2} + C_\infty
\] (3.13)

and:

62
\( C_\infty = \frac{C_s C_p}{C_s + C_p} \)  

(3.14)

at the characteristic frequency defined as:

\[
v_0 = \frac{2R_s + R_p}{2\pi R_s R_p (C_s + C_p)} \]

(3.15)

From this expression, we can therefore calculate the complex dielectric constant of the system, taking into account the following relationships:

\[
\varepsilon_0 \Delta \varepsilon = \frac{\Delta C}{t} \quad \quad \varepsilon_0 \varepsilon_\infty = \frac{C_\infty}{t}
\]

and thus we can obtain a Debye type expression related to the effective dielectric constant of the system as follow:

\[
C(v) = \frac{\Delta C}{1 + \left( \frac{v}{v_0} \right)^2} + C_\infty = \varepsilon_0 t \left( \frac{\Delta \varepsilon}{1 + \left( \frac{v}{v_0} \right)^2} + \varepsilon_\infty \right)
\]

(3.16)

By developing all the terms of this expression for resistance and capacitance values, it is possible to calculate the dielectric constant of the system by using the respective values of \( R_s \), \( C_s \), \( R_p \) and \( R_s \) shown in Fig (3.7 (c)) we obtain:

\[
\Delta \varepsilon = \frac{\varepsilon_p \frac{t}{\delta} + \varepsilon_s \left( \frac{\sigma_p t}{\sigma_s \delta} \right)^2}{1 + \left( \frac{\sigma_p t}{\sigma_s \delta} \right)^2}
\]

(3.17)

and the characteristic frequency of relaxation:
\[ \nu_0 = \frac{1}{2\pi \varepsilon_0} \frac{\sigma_s + \sigma_p T}{\varepsilon_s + \frac{\varepsilon_p T}{\delta}} \]  

(3.18)

And

\[ \varepsilon_\infty = \frac{2\varepsilon_s \varepsilon_p \frac{T}{\delta}}{2\varepsilon_s + \varepsilon_p \frac{T}{\delta}} \]  

(3.19)

With the hypothesis \( t >> \delta \) and the conductivity of the GO particle \( \sigma_p \rightarrow 0 \) we can therefore determine the amplitude and frequency of the dielectric relaxation and the dielectric constant at high frequency.

\[ \Delta \varepsilon^\parallel = \varepsilon_p \frac{T}{\delta} \]  

(3.20)

\[ \nu_0^\parallel = \frac{\delta \sigma_s}{2\pi \varepsilon_0 \varepsilon_p} \]  

(3.21)

\[ \varepsilon_\infty^\parallel = \varepsilon_s \]  

(3.22)

Regarding the system with the GO particles oriented with their normal planes perpendicular to the direction of the electric field we obtain another RC circuit with its elements in parallel showed in Figure (3.8 (b)).
Figure 3.8 – (a) Schematic sketch of a cubic cell consisting of insulating GO flakes in the solvent with the direction of their normal perpendicular to the electric field. (b) RC model associated in terms of $R_s$, $C_s$, $R_p$ and $C_p$. (c) Resistance and capacitance of the particles and solvent expressed in terms of $t$ and $\delta$ for system in which the normal of the particles is parallel to the direction of the electric field.

Also in this case, the complex capacitance of the system can be expressed starting from the complex impedance expressed through the respective resistance and capacitance values of the associated RC circuit:

$$Z_1^* = \frac{1}{R_s} + jC_s \omega$$  \hspace{1cm} (3.23)

and

$$Z_2^* = jC_p \omega$$  \hspace{1cm} (3.24)

From the impedances of the respective components related to the solvent and the GO particle we obtain:

$$\frac{1}{Z_{tot}^*} = \frac{1}{R_s} + j \omega (C_p + C_s)$$  \hspace{1cm} (3.25)

with,

$$(C_p + C_s) = \varepsilon_{eff} = \varepsilon_0 \varepsilon_s t + \varepsilon_0 \varepsilon_p \delta$$  \hspace{1cm} (3.26)
and

\[ \Delta C_{eff} = \varepsilon_0 \varepsilon_p \delta = C_p \tag{3.27} \]

Figure 3.9 – Schematic representation of the effective capacitance according to the frequency.

Considering the cubic geometric of the system we obtain the following expression for \( C_{eff} \) :

\[ C_{eff} = \frac{\varepsilon_0 \varepsilon_{eff} t^2}{t} = \varepsilon_0 \varepsilon_{eff} t \tag{3.28} \]

with:

\[ \varepsilon_{eff} = \frac{\varepsilon_0 \varepsilon_s t + \varepsilon_0 \varepsilon_p \delta}{\varepsilon_0 t} \tag{3.29} \]

and, being \( t \gg \delta \):

\[ \varepsilon_{eff} = \frac{\delta \varepsilon_p + \varepsilon_s t}{t} = \varepsilon_s + \varepsilon_p \frac{\delta}{t} \tag{3.30} \]

From these expressions, we can easily predict the trend of \( \varepsilon_{eff} \), as well as previously for \( C_{eff} \).
Chapter III  

Electrostrictive soft material for sensing and mechanical energy harvesting

Figure 3.10 – Schematic representation of the effective capacitance according to the frequency.

Figure 3.11 – Variation of permittivity of a lamellar system as a function of frequency for two limit cases of orientation with respect to the electrical field. In detail it is possible to observe a Debye-type relaxation with a wide amplitude, for the system that presents the normal of GO flakes parallel to the electric field direction and a flat behavior for the system that presents the normal of GO flakes perpendicular to the electric field direction.
3.6 – Results and Discussion

3.6.1 – Flow dependent measurements

Figure 3.9 shows the flow dependent dielectric spectroscopy of GO dispersion 0.4 wt% in Milli-Q water over the whole investigated frequency range. To verify the sensitivity of our samples to an external mechanical stress and therefore their electrostrictive properties, we performed flow dependent measurements, at low flow velocity (up to 1000 µL/min). For clarity, here we show only the results obtained at flow rates of 300 µL/min and 1000 µL/min. Specifically, in Figure 3.9 we report the capacitance and the AC conductivity of GO at 0.4 wt% (biphasic state).

Being similar with the phenomenon reported in the literature, in Figure 3.9 (a) we find a giant capacitance at low frequency for the GO dispersion in static conditions. This relaxation could be well explained by the relaxation model previously mentioned for platelets in solution. However, we will see in the next chapter that this relaxation may have a different origin.

From Figure 3.9 (a) it seems evident that the effect of the flow does not induce a variation in the dielectric properties of the sample, by contrast to what we expected. To understand the origin of this result, a more accurate analysis of the nature of the flow is needed. It might be possible in fact that the mechanical stress produced by flow applied in our experiments is too low to alter the structural orientation of the flakes.

Considering the specific section of the dielectric cell, a flow rate of 1000 µL/min corresponds to a low shear rate. To rule out the extent of the flow rate as a possible cause for these results, we also performed the same measurements at higher flow rates, but no substantial differences in the dielectric properties have been detected. Therefore, we decided not to show the results in this manuscript, since they go beyond the purpose of this work. Figure 3.9 (b) shows the AC conductivity relative to a GO 0.4 wt% dispersion in Milli-Q water. This measurement is totally dominated by the ionic contribution showing an almost flat behavior around $10^{-2}$ S/m.
Figure 3.9 - Frequency dependence of capacitance (a) and AC conductivity (b), of a GO dispersion 0.4 wt% in milli-Q water in static and dynamic conditions. Black circles shows the trends in static condition, whereas the red continuous line and the green dotted line represent the measurements in dynamic conditions at 300 µL/min and 1000 µL/min, respectively. (Error bar 10%)

Differently from the dielectric properties, here it is possible to observe an effect of the flow in the dynamic measurements, with an average decrease of the conductivity of 17%, compared to the static value, at the flow rate of 300 µL/min and of 33% at highest flow rate (the variation has been measured at 1 kHz).

This decrease could be attributed to the fact that the flow direction is perpendicular to the direction of the electric field and thus to the direction of conductivity measurements. However, the origin of this decrease is still unclear. We speculate that it could be due to an enhanced alignment of the GO flakes under flow.

Actually, it was shown in Rheo-SAXS experiments that the fraction of aligned flakes parallel to the flow increases with increasing shear rate $^{[33]}$. In such conditions, the GO flakes can act as more efficient barriers towards the motion of ions along the electric field. This hypothesis of course requires deeper study to be validated. Nevertheless, we can already observe experimentally that this sensitivity to flow can be an opportunity for making original fluid piezo-resistive sensors.

The flow dependent dielectric spectroscopy for a GO 0.4 wt% dispersion in Isopropyl alcohol, reported in figure 3.10, gives similar results. The capacitance in Figure 3.10 (a) shows a similar trend observed also in Milli-Q water.
Figure 3.10 - Frequency dependence of capacitance (a) and AC conductivity (b) of a GO dispersion 0.4 wt% in Isopropyl Alcohol in static and dynamic conditions. Black circles show the trends in static condition, whereas the red continuous line and the green dotted line represent the measurements in dynamic conditions at 300 µL/min and 1000 µL/min, respectively. (Error bar 10%).

In particular, we report a high value equal to 270 pF at 1 kHz. The AC conductivity measured here is significantly lower than the one measured in Milli-Q water, but also in this case the measurement is dominated by the ionic conduction and thus by the free charge carriers in the dispersion. The conductivity slightly increases with the frequency. From Figure 3.10 (b), we can find values of about $10^{-4}$ S/m in static conditions and decrease of 11% at 300 µL/min and of 29% at 1000 µL/min.

### 2.6.2 – Shear induced birefringence analysis

The impossibility of tuning the dielectric properties in dynamic conditions drove us to carry out an accurate analysis of the effect of the flow on the physical structure of our system. For this purpose, we used polarizing optical microscopy to monitor the birefringence variation of the dispersion under flow. Figure 3.6 (b) shows the specific home-built macrofluidic device realized to perform this specific analysis. The device is composed of two glass plates separated by a layer of polydimethylsiloxane (PDMS). The inlet and the outlet for the connection with a syringe-pump are placed at the top of the device. The geometry of the channel (500 µm in thickness, 4 mm in width) corresponds to that of the dielectric cell.
The orientation of LCs in general is strongly influenced by the boundary conditions of the substrates, confinement and anchoring, because they interact with the confining surfaces. As can be seen in Figure 3.6 (a), polarizing microscopy reveals that GO flakes align in a pseudo-lamellar phase in a confined space. In fact, the uniform dark area indicates a homogeneous alignment of the director $n$, the unit vector that specifies the nematic alignment of the flakes, with GO flakes parallel to the confining glass plate. Along the edges, it is possible to observe a white area due to a different orientation of the flakes due to the interaction with the hydrophobic PDMS substrate.

When the GO flakes align at different angles with respect to the director $n$ of the domains with the axes of the polarizer, a variation of birefringence should be expected. Figure 3.11 shows the evolution of the birefringence, and therefore the light and dark areas, depending on the orientation of the director $n$.

It is important to note how the black area is given by a perfect alignment of the flakes with the director at 0° or at 90° with respect to the axes of the polarizer.

Figure 3.11 - Schematic sketch of the evolution of local orientation of the director $n$ through the axes of polarizer

Figure 3.12 shows the shear-induced birefringence of GO dispersion at 0.4 wt% in Milli-Q water in static and dynamic conditions (at various flow rates). As the flow-rate increases, a slight variation in the birefringence of the dispersion is visible. This suggests that the flow rates applied are not effective enough to alter the local orientation of the flakes, potentially explaining the lack of variation in the dielectric properties of the medium.
In order to foster an increase of the structural variation of the flakes under dynamic conditions, we use a multi-tips mask to perform the same analysis. The presence of obstacles in the mask inserted in the dielectric cell creates distortions that make the flow deviate from parallel conditions.

Figure 3.14 shows the shear-induced birefringence analysis for a GO 0.4 wt% dispersion in Milli-Q water in response to an obstacle.
Figure 3.14 – Shear induced birefringence analysis for a sample of GO 0.4 wt% dispersions in Milli-Q water in static and in dynamic condition in presence of an obstacle (scale bar 2500 µm).

Being different from the “pure” parallel conditions, here the flow rate has a higher impact on the birefringence. The obstacle, in fact, forces the local orientation of the flakes during the movement in the channel\textsuperscript{[38,39]}. Although the nature of the flow remains complex, near the obstacle polarized microscopy shows a bright area, due to the alteration of the orientation of the flakes between 0° and 90° with respect to the axes of the polarizers.

The presence of the multi-tips mask should therefore accentuate this effect given the presence of more obstacles. A further confirmation of the increased variation of birefringence is obtained through an analysis of the histogram of the images, where 0 represents the less exposed pixels (black areas) and 255 is the maximum exposition (white areas). In our case, the exposition is strictly related to the orientation of the flakes, as seen in figure 3.15. For simplicity, we report only the flow-rates at 300 and 1000 µL/min. In Figure 3.15 it is possible to observe a peak at zero due to the abundance of black area in static conditions, regardless of the configuration used\textsuperscript{[40-42]}. This peak is due to the specific orientation of the flakes in a pseudo-lamellar phase.
As the flow rate increases, the peak moves towards lighter areas for the two configurations, even if the effect is enhanced by the presence of the obstacles, where the variation of birefringence is around 20% compared to the static conditions. This result seems promising concerning the flow dependent dielectric measurements by using the multi-tip mask.

Figure 3.15 – Shear induced birefringence analysis for a sample of GO 0.4 wt% dispersions in Milli-Q water in static and in dynamic condition in presence of an obstacle (scale bar 2500 µm) (A) without obstacle, (B) in presence if an obstacle. Analysis of the histogram of the photographers of shear-induced birefringence. (C) Without obstacle, (D) in presence of an obstacle.

2.6.3 – Flow dependent measurements with multi-tips mask

In light of the results obtained by polarized microscopy, we decided to perform flow-dependent dielectric measurements using the multi-tips mask. The insertion of the mask in the cell does not alter the electrical measurements, as the electrode-related areas are well distanced from the obstacles. As already presented in paragraph 3.5.1, we will report the experiments for GO dispersions in Milli-Q water and Isopropyl Alcohol.
From Figure 3.16 (a) it is clear that the flow does not have an effect on the capacitance of a dispersion of GO 0.4% in Milli-Q water.

Furthermore, the capacitance is high at low frequency, as already reported in literature. Figure 3.16 (b) shows AC conductivity of the sample. Here the presence of the mask implies a different variation with respect to the measurements made in the absence of these, due to
fluctuations of the conductivity value under flow. In detail, the flow measurement, relative to 300 µL/min shows a decrease of 13% while the flow measurement relative to 1000 µL/min shows a decrease of 37% (both variations are recorded at 1 KHz).

For GO 0.4 wt% in Isopropyl alcohol, we found the same result; the flow does not alter the capacitance of the system, as shown in figure 3.17 (a). As previously stated, the introduction of the multi-tip mask induces fluctuation in the measurement of the conductivity under flow, with a decrease of 28% at 300 µL/min and 36% for the highest flow-rate compared to the value in static conditions.

2.7 – Conclusion

GO dispersions show high capacitance at low frequencies compared to high frequencies in both Milli Q-water and Isopropyl Alcohol, as confirmed by dielectric spectroscopy. In particular, it was measured capacitance values in the µF for the dispersion in milli-Q water and values in the nF for the Isopropyl alcohol. This difference between the two values can be attributed to the different polarity of the two solvents. Knowing that the dielectric properties of system are related to their structural arrangement we decided to investigate the properties of GO dispersion in dynamic conditions, under flow.

We observed no effect of flow in the dielectric properties of the system in spite of orientation changes of the flakes. By introducing one obstacle in the channel to increase the tortuosity, the birefringence under flow increases above 20 % compared to the static conditions, as shown by polarized light microscopy. Unfortunately, introducing a multi-tips mask in the cell for electrical measurements do not improve or show any significant variation in the dielectric properties of the dispersions under flow.

From this evidence, we deduce that the systems may not be suitable for energy harvesting applications in variable capacitors. However, we observe a significant variation in the conductivity of the dispersions. Therefore, they may be suitable for sensing applications using original and stable piezo-resistive fluids. The origin for the variations of conductivity under has to be clarified.

This unexpected result led us to reconsider the intrinsic dielectric constant of the particle. For this reason, a detailed analysis of the dielectric properties of GO dispersions in polar solvents will be presented in the following chapter.
Reference


[34] Zhang, W.L.; Choi, H.J. Graphene Oxide Based Smart Fluids. *Soft Matter* 2014, 10, 6601.


Chapter IV

Dielectric Spectroscopy of GOLC dispersions
4.1 – Introduction

Graphene oxide (GO) is considered as a promising material for electronics and energy storage applications, in which high-permittivity materials are sought after. According to various studies, in fact, GO could display a giant permittivity. For example, Liu et al. [1] reported that GO can be used as a high-\(k\) material for energy storage applications with a dielectric constant higher than 1000 at 100 Hz. Hong et al. drew the same conclusion [2] and Huang et al. [3] reported values of relative permittivity above 100 at 100 Hz.

Concerning Graphene Oxide liquid crystals (GOLCs), K. Kumar et al. [4] found even greater values, up to \(10^6\) at 1 kHz, and suggested that this giant dielectric constant arises from the orientation polarization of oxygen-containing groups at the surface of GO planes and along the edges as shown in Figure 1 [4,5].

![Schematic image of a GO flake](image)

**Figure 4.1** – Schematic image of a GO flake where the black circles shows the conductive regions dominated by a \(sp^2\) character and the polar regions due to the functionalization.

Very large dielectric constants have also been reported for GO based foams and sensors even in absence of humidity [5,7]. Similar results have also been suggested from characterizations of composite materials in which a small fraction of GO added to a polymer enhances the effective permittivity of the composites [14–20]. By contrast, other studies
reported more moderate values of dielectric constants (around 3 or less), in frequency ranges typically from 100 to 1 KHz [8-10]. Uses of GO as dielectric material in transistors led also to the conclusion that GO has a relative permittivity typically between 3 and 5 [11-13].

The actual value of the GO permittivity still remains unclear, and this uncertainty is even more evident for GO materials in solution. Al-Zangana et al. [21] have recently investigated dielectric relaxation processes of GO solutions in isotropic fluids or liquid crystal states. Relaxations in isopropyl alcohol are associated with very large amplitudes, well above 1000 in relative permittivity, at 1 kHz.

Again, such giant amplitudes would reflect a giant intrinsic dielectric constant of GO particles. The same conclusion would hold for various GO polymer composites developed for energy storage applications, which display very large effective dielectric constants.

Nevertheless, we have to keep in mind that the large permittivities reported in literature, are all deduced from capacitance measurements in complex electrical circuits. As already discussed by some authors [14,16], other mechanisms, and in particular polarization of electrodes could contribute to the measured capacitance, but this contribution was often considered as negligible.

Actually, differentiating the contribution of the electrode polarization from bulk polarization is challenging, and a direct comparisons of GO with other graphitic materials could be irrelevant, because GO, unlike graphene or other graphitic particles, can be considered as a polyelectrolyte which carries a huge number of counter-ions. The latter, both in liquids or polymers, can form ionic double layers at the surface of the electrodes and generate a large double layer capacitance, which alters the dielectric behavior of the samples examined.

In order to clarify the situation, and determine whether GO displays a giant permittivity or not, we propose in this work a simple approach, which consists in measuring the capacitance of dielectric cells filled with GO solutions at different concentrations.

In particular, we corrected the measured impedance by taking into account the contributions of both the sample-holder and the coaxial cables and using an equivalent electrical circuit model that considers the contribution of both the electrodes polarization and the dielectric medium.

As previously observed in literature, experiments in both Milli-Q water and isopropyl alcohol confirm the measurements of very large capacitance. However, by interpreting these results
with our simple model, we demonstrate that the observed capacitances are not due to a strikingly high permittivity of GO or to specific relaxation modes related to the rotation of the particles \cite{21}. They can instead be easily explained by considering the polarization of electrodes. In light of this new interpretation, we therefore conclude that GO is not a high permittivity material with a potential application in dielectric energy storage systems, electrostrictive sensors or energy harvesters \cite{1,7,17-19}.

**4.2 – Electrode Polarization**

Dielectric spectroscopy (DS) is a powerful technique to study the dynamic and kinetic processes occurring in soft condensed matter in a wide range of frequencies. Being broadband techniques sensitive to dipolar motions, these techniques would seem to be suited for the investigation of GOLCs, due to the polar nature of these systems. GOLCs always contain a certain amount of ionic contaminants, which affect the determination of their dielectric properties due to the formation of spatial charge regions in proximity of the electrode (metal/solution interphase), called electrode polarization (EP). When an external alternating electric field is applied, the charge carriers drift towards the electrode/solvent interface forming an electric double layer, and therefore enhancing polarization phenomena.

![Figure 4.2 – Schematic representation of the formation of ionic double layers at the electrode/sample interfaces and of EP effect in a measured signal \cite{22}.](image)

At low frequencies, the inversion of the electric field is too slow to allow electric charges to move away from the interphase of the electric double layer and the polarization effect is
higher. By contrast, at high frequencies the polarity inversion is fast enough to keep the charge carriers in a steady state and not anchored to the electric double layer.

GO flakes and their counter-ions are easily adsorbed at interfaces, and they can form a strong electric double layer near the electrode, together with their counter-ions, giving rise to a high capacitance at the interface. If these strong EP effects are not taken into account in data treatment, the interpretation can lead to misleading results, like an apparently giant dielectric constant of the sample.

4.2 – Equivalent Electrical Circuit Model

Alternative current (AC) measurements allow for analyzing the frequency dependence of the real and imaginary part of impedances correlated to the contribution of conductance and reactance of the sample. In order to discriminate between the contribution of electric double-layer capacitance and the bulk properties and to do quantitative analysis of the system, we used a simple equivalent electrical circuit model, which reproduces the experimental impedances of the dispersions.

![ Equivalent Electrical Circuit Model](image)

Figure 4.3 – Schematic sketch of the equivalent electrical circuit model for a two-planar heterogeneous layer system, whose longitudinal direction is perpendicular to the direction of the electric field.

In literature, there are several models for carbon-based materials and graphene-based liquid crystals, that differ in complexity and are suitable for a broad frequency range\[^{23}\].

Our model, shown in Figure 4.3, consists of a finite diffusion Warburg element $W$ to account for the diffusion of charged species through the liquid crystal, whose impedance is defined as $Z_w = w(1 - j)\omega^{-1/2}$\[^{24}\].
The latter, is connected in series to a resistor $R_{pol}$ that models the resistance of polarization of electrodes. Both $W$ and $R_{pol}$ are in parallel with a capacitor $C_{dl}$ that models the accumulation of charges at the interface for an adsorbed double layer capacitance. In parallel to the latter, a capacitor $C_{bulk}$, that represents the contribution of the bulk dispersions and is linked to the actual relative permittivity of the sample and a resistor $R_{disp}$ connected in series, that represents the resistance of bulk dispersions due to the ionic species (a measure of the conductivity of the sample).

As shown further, such equivalent electrical circuit model gives a satisfying accuracy for high frequency values between 100 Hz and 1 MHz.

The total impedance of the equivalent circuit will be calculated from the impedance of its components.

![Equivalent Electrical Circuit](image)

**Figure 4.4 – Equivalent electrical circuit (EEC) of the sample.** The circuit comprises a finite diffusion Warburg element $W$, in series with a resistor $R_{pol}$. Both of them are in parallel with a capacitor $C_{dl}$ as described in the classic Randles cell model \(^{(25)}\). In addition, a resistor $R_{disp}$ represents the resistance of bulk dispersion and a capacitor $C_{bulk}$ in parallel describes the effective capacitance of the bulk dispersion.

### 4.4 – Results and Discussion

The experimental electrical impedances were compared with the theoretical values obtained using the equivalent electrical circuit model, keeping its elements constant over the whole frequency range.

Figure 4.5 shows the frequency dependence of the real and imaginary part of the impedance for GO dispersions in Isopropyl Alcohol (IPA). The simulated impedance (solid line) well
match the experimental impedances of the samples at different GO concentrations (colored circles), suggesting that the proposed model is suitable and accurate enough to describe the electrical behavior of the samples. This procedure allows us to determine the bulk capacitance of the GO dispersions in comparison to that of the supernatant and therefore to estimate the intrinsic permittivity of the GO particle.

The real part of the impedance for dispersions in Isopropyl Alcohol, as can be seen in Figure 4.5 (a), decreases by an order of magnitude with increasing concentrations of GO. This trend reflects how the resistance $R_{disp}$ of the samples decreases with the increase of the GO flakes concentration.

Figure 4.5 - Frequency dependences of the real (a) and imaginary part (b) of measured impedance for GO dispersions in Isopropyl Alcohol. The colored circles represent the experimental values whereas the continuous lines show the simulated data for the concentrations: 0.4 wt% (red), 0.6 wt% (green), 1.0 wt% (blue), 1.5 wt% (magenta), 3.0 wt% (orange), 6.5 wt% (pink) and the respective supernatant (Black).

<table>
<thead>
<tr>
<th></th>
<th>$R_{pol}$ [Ω]</th>
<th>$W_{0.5}$ [Ω]</th>
<th>$C_{dl}$ [F]</th>
<th>$R_{disp}$ [Ω]</th>
<th>$C_{Bulk}$ [F]</th>
</tr>
</thead>
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<tr>
<td>Supernatant</td>
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<td>14000</td>
<td>1.00e-9</td>
<td>61000</td>
<td>3.05e-11</td>
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<td>18000</td>
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<td>30500</td>
<td>3.80e-11</td>
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<tr>
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<td>14000</td>
<td>1.50e-9</td>
<td>20300</td>
<td>4.00e-11</td>
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<td>13700</td>
<td>4.20e-11</td>
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<tr>
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<td>5.00e-11</td>
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<td>7000</td>
<td>2.50e-9</td>
<td>3070</td>
<td>5.80e-11</td>
</tr>
</tbody>
</table>

Table 3.1 – The values of each element of the EEC model that give the best fitting for a GO dispersion in Isopropyl Alcohol.
The imaginary part of the impedance, shown in Figure 4.5 (b), also decreases as the concentration of the GO flakes increases, showing a maximum peak starting from 10 kHz, which reflects a capacitive mode behavior. These peaks shift at high frequency with the concentrations.

Figure 4.6 - Resistance of the bulk dispersions and AC conductivity (a) and Capacitance values of $C_{UL}$ and $C_{bulk}$ (b) as function of concentration for GO dispersions in Isopropyl Alcohol. (Error bar 10 %)

Figure 4.6 (a) shows the trends of the bulk resistance, $R_{disp}$, and the related AC conductivity calculated through the following expression:

$$AC \sigma = \frac{d}{R_{disp} A}$$  \hspace{1cm} (4.1)

with, $d$ equal to 500 μm and $A$ equal to 96 mm$^2$. The progressive increase in conductivity with GO concentrations shows how the GO particles behave as a pure electrolyte in solution. Concerning the capacitive behavior, by using the values obtained from the fitting, we identified the two contributions to the total capacitance: interface capacitance and bulk capacitance.

In details, it is possible to observe the large difference between them as shown in Figure 4.6 (b). In fact, as the GO concentration increases, the electric double layer capacitance increases significantly even for small concentrations of GO. Specifically, from 1 nF, relative to the supernatant, to 2.5 nF for a concentration of 6.5 wt%, whereas the bulk capacitance evolves from 30 pF, relative to the supernatant, to 58 pF for a concentration of 6.5 wt%. 

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The relative permittivity of the samples can be deduced from the capacitance of the bulk using equation 4.2

\[ C_{\text{Bulk}} = \varepsilon_0 \varepsilon_r \frac{A}{d} \]  

(4.2)

In Figure 4.7 it is possible to observe how the permittivity of the dispersions grows with the concentration of GO. This increase is clear but not as large as the increase which could have been expected if GO would have had a giant permittivity.

As mentioned in the previous chapter, the GOLCs systems can be considered as a heterogeneous system of planar-2D particles in a pseudo lamellar phase in which the amplitude \( \Delta \varepsilon \) (the difference between the \( \varepsilon_r \) of GO at 6.5 wt% and the one of the supernatant) is related to the dielectric constant of the particles \( \varepsilon_p \) as follow (see previous chapter):

\[ \Delta \varepsilon = \varepsilon_p \frac{t}{\delta} \]  

(4.3)

where, \( t \) is the thickness of the solvent layer and \( \delta \) the thickness of the particle. Using this relation, we can estimate the value of the dielectric constant of the particle.

![Figure 4.7](image-url) - Deduced permittivity of the dispersions as function of concentration for GO dispersions in IPA. (Error bar of 21%).
The ratio of the respective thickness of the GO layer and solvent layer can be estimated through the volume fraction $\phi_V$, defined by the ratio of the volume of the particle and the total volume.

$$\delta/t \sim \phi_V \quad (4.4)$$

From this relation, by using the respective density of the solvent equal to 0.79 g/mL and 1.83 g/mL for GO we obtain a value of $\phi_V \sim 0.0291$ which reflect a value for the dielectric constant of the particle equal to $\sim 0.98$ for the dispersions in Isopropyl Alcohol (the estimated value considers the propagation of errors).

<table>
<thead>
<tr>
<th></th>
<th>Supernatant</th>
<th>GO 0.4 wt%</th>
<th>GO 0.6 wt%</th>
<th>GO 1.0 wt%</th>
<th>GO 1.5 wt%</th>
<th>GO 3.0 wt%</th>
<th>GO 6.5 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\text{bulk}}$ [F]</td>
<td>3.05e-11</td>
<td>3.80e-11</td>
<td>4.00e-11</td>
<td>4.20e-11</td>
<td>4.60e-11</td>
<td>5.00e-11</td>
<td>5.80e-11</td>
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<tr>
<td>$\varepsilon_r$</td>
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<td>22.36</td>
<td>23.54</td>
<td>24.71</td>
<td>27.07</td>
<td>29.42</td>
<td>34.13</td>
</tr>
</tbody>
</table>

Table 3.4 – Capacitance of the bulk of the dispersions and relative permittivity of GO Isopropyl Alcohol.

Figure 4.8 - Frequency dependences of the real (a) and imaginary part (b) of measured impedance for GO dispersions in Milli-Q water. The colored circles represent the experimental values whereas the continuous lines show the simulated data for the concentrations: 0.4 wt% (red), 0.6wt% (green), 1.0 wt% (blue), 1.5 wt% (magenta), 3.0 wt% (orange), 6.5 wt% (pink) and the respective supernatant (Black).
Concerning the GO dispersions in Milli-Q water, the behaviors of the real and imaginary parts of the impedance are slightly different. This can be attributed to the higher polarity of the solvent. In detail, real part of the impedance, shown in Figure 4.8 (a), decreases with the GO concentration.

<table>
<thead>
<tr>
<th></th>
<th>( R_{\text{pol}} ) [( \Omega )]</th>
<th>( W ) [( \Omega )^{-0.5}]</th>
<th>( C_{\text{dl}} ) [( \text{F} )]</th>
<th>( R_{\text{disp}} ) [( \Omega )]</th>
<th>( C_{\text{Bulk}} ) [( \text{F} )]</th>
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<tr>
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<td>6.0e-10</td>
<td>500</td>
<td>1.40e-10</td>
</tr>
<tr>
<td>GO 0.6 wt%</td>
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<td>5.0e-8</td>
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<td>1.43e-10</td>
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<td>8.2e-8</td>
<td>207</td>
<td>1.45e-10</td>
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<tr>
<td>GO 1.5 wt%</td>
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<td>8.5e-8</td>
<td>123</td>
<td>1.47e-10</td>
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<tr>
<td>GO 3.0 wt%</td>
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<td>GO 6.5 wt%</td>
<td>1</td>
<td>1250</td>
<td>1.0e-7</td>
<td>36</td>
<td>1.65e-10</td>
</tr>
</tbody>
</table>

Table 3.5 – The values of each element of the EEC model that give the best fitting for GO dispersions in Milli-Q water.

This result reflects a decrease of resistance of the bulk, which confirms again that GO acts as a simple electrolyte in solution. In addition, the real part of the impedance in Milli-Q water, shows a relaxation at frequency higher than 1 MHz, in agreement with other studies \(^{[26]}\). The lack of relaxation in the investigated range of frequencies entails to a large uncertainty of the fitting. However, since the relaxation of the real part occurs at frequencies higher than 1 MHz, the maximum point of the imaginary part, showed in Figure 4.8 (b) is not completely visible in the investigated frequency range.

Figure 4.9 (a) shows the trends of the bulk resistance, \( R_{\text{disp}} \), and the related AC conductivity for a GO dispersion in Milli-Q water. Also in this case, the progressive increase in conductivity with GO concentrations reflects the tendency of GO particles to behave as a simple electrolyte in solution.

In detail, the conductivity of the bulk dispersions shows a linear variation evolving in average by two orders of magnitude from the supernatant to the highest concentrations of GO equal to 6.5 wt%.
By using the values obtained from the fitting, we can identify the two contributions to the total capacitance, shown in Figure 4.9 (b), as we did for the systems in Isopropyl Alcohol. As the GO concentration increases, the electric double layer capacitance increases clearly even for small concentrations of GO, below the critical concentration of isotropic-nematic transition, and then it becomes constant at high concentrations.

![Figure 4.9](image)

Figure 4.9 - Resistance of the bulk dispersions and AC conductivity (a) and Capacitance values of $C_{\text{DL}}$ and $C_{\text{bulk}}$ (b) as function of concentration for GO dispersions in Milli-Q water. (Error bar 10 %)

<table>
<thead>
<tr>
<th></th>
<th>Surnatant</th>
<th>GO 0.4 wt%</th>
<th>GO 0.6 wt%</th>
<th>GO 1.0 wt%</th>
<th>GO 1.5 wt%</th>
<th>GO 3.0 wt%</th>
<th>GO 6.5 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\text{DL}}$ [F]</td>
<td>1.36e-10</td>
<td>1.40e-10</td>
<td>1.43e-10</td>
<td>1.45e-10</td>
<td>1.47e-10</td>
<td>1.55e-10</td>
<td>1.80e-10</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>80.37</td>
<td>82.39</td>
<td>84.15</td>
<td>85.33</td>
<td>86.51</td>
<td>91.21</td>
<td>105.93</td>
</tr>
</tbody>
</table>

Table 3.7 – Capacitance of the bulk of the dispersions and relative permittivity of GO Milli-Q water.

In details, the interface capacitance evolves from 0.5 nF, relative to the supernatant to 100 nF for a dispersion of 6.5 wt%. By contrast, the bulk capacitance, referred to the dielectric properties of the sample, evolves from 136 pF relative to the supernatant to 180 pF for the highest GO concentration.

As previously done for the dispersion of GO in isopropyl Alcohol, we calculated the value of the permittivity of GO dispersions in Milli-Q water using equation (4.2). It is necessary to note that the lack of relaxation of the real part of the impedance and the consequent absence of a maximum peak in the imaginary part entail a certain degree of uncertainty in the fitting which can lead to an overestimation of the intrinsic permittivity of the particles.
Nevertheless, according to the results obtained, we can confirm that the inclusion of GO does not alter significantly the permittivity of the dispersions, even at high concentrations. Using equation 4.3, and the volume fraction for Milli-Q water, equal to $\phi_V \sim 0.0361$, we found a value of 2.33 for the dielectric constant of the GO particle in Milli-Q water (the estimated value considers the propagation of errors).

In any case, even if the two values found in Milli-Q water and IPA are just estimates of the dielectric constant of the particle, they are still significantly lower than the giant permittivity found in many other papers [1-5,21].

4.5 – Conclusions

During direct measurements of the capacitance, the strong polarization of the electrodes alters the determinations of the dielectric properties of the samples. To take into account this effect, we proposed an equivalent electrical circuit model, in order to perform a more accurate quantitative analysis of the system and to distinguish the contribution of electric double-layer capacitance from the bulk properties, which reflect the true dielectric properties of the systems.

The experimental electrical impedance was compared with the theoretical values, keeping the elements of this circuit constant over the whole frequency range.
According to the results obtained by using the model and regardless of the solvent used to disperse GO flakes, the main contribution to the experimentally observed capacitance is given by the electrical double layer (of the order of nF) of the electrodes, whereas the bulk capacitance is significantly lower (in the order of pF). As a matter of fact, the dielectric constant of GO dispersions derived from these values is just slightly higher than the dielectric constant of the supernatant. Therefore, we do not consider GOLCs as good candidates for high-k materials. Nevertheless, GO can be used as component for devices that exploit an interphase capacitance, like Field Effect Transistors (FETs) or as an electrolyte and precursor for graphene based materials, but not as an additive to raise the permittivity of solvents and composites for electronics (capacitive sensing, and energy harvesting in variable capacitors) and energy storage applications.
Chapter IV

Dielectric spectroscopy of GOLCs dispersions

References


Chapter V

Electrochemical Flow Capacitors
5.1 – Introduction

Recently, there has been a growing interest in making energy more accessible and sustainable. Scientific research has undertaken new challenges for the management and implementation of the energy net with new technologies that exploit renewable energy, as widely discussed in this thesis \[^{1,2}\]. Nowadays, there are different energy storage and conversion technologies, which offer a wide range of energy and power densities; therefore, they can be employed in several applications \[^{3,4,5}\].

As we discussed in chapter I, electrochemical energy storage devices show high versatility and can guarantee performances that meet most of the standard energy demand. Furthermore, the characteristic of these devices can be optimized, representing an excellent perspective for the future. In this regard, a few years ago, the team of Drexel Nanotechnology Institute of Professor Yuri Gogosti presented a new concept of energy storage technology for grid-scale capacitive energy storage, known as electrochemical flow capacitor (EFC) \[^{6,7}\]. This new technology benefits from the advantages of both flow batteries and supercapacitors, since it is based on the same fundamental principles. EFCs allow for quick charge and discharge processes, have a long-life cycle, and, by controlling the size of the system, are able to store energy for different applications. The architecture of EFCs, showed in Figure 5.1, is similar to that of redox flow batteries, consisting of an electrochemical flow cell with two channels that are separated by an electrically insulating membrane; the cell is connected to an external circulatory system of pumps and vessels, which contain the active materials. The principle of operation is simple and shares common features with that used in redox flow \[^{8}\], liquid metals \[^{9}\] or semi-solid flow batteries \[^{10}\].

In contrast to the traditional flow-assisted electrochemical energy storage systems (FAES), in which the electroactive material is a liquid redox electrolyte, EFCs work with a flowable capacitive dispersion of porous carbon particles suspended in an electrolyte, which represents the main novelty of these systems. Similar to conventional supercapacitors with a solid-state electrode, these aqueous based slurries are limited in terms of energy density when compared to batteries, but the quick charging process allows for the decoupling of the power output and energy storage, overcoming the major limitation of supercapacitors \[^{11}\].

Nowadays, several research groups are trying to increase the energy density of flowable
carbon dispersions through pseudo-capacitive processes \cite{12}, or using organic electrolytes to increase the voltage windows applied \cite{13}.

The operating principle of EFCs is based on charge-discharge cycles of the carbon dispersion under flow conditions. During the charging process, the uncharged carbon dispersion flows inside the electrochemical cell separated into the two channels. When an external bias is applied, the dispersion becomes polarized either positively or negatively, depending on the channel in which it is flowing, because of the formation of an electrical double layer on the surface of the active material and the dissolved electrolyte. The charge balance during this process is ensured by the diffusion of the electrolyte ions through the membrane. Once the slurries are charged, they are stored in two separate vessels. In each vessel, the total charge is close to zero as the electric charge on the active material is balanced by ions of opposite charge.

![Diagram of EFCs operation](image)

**Figure 5.1 – Scheme of EFCs operation.** Uncharged carbon slurry is pumped from storage vessels into an electrochemical flow cell in the charging process. Fully charged carbon dispersion is then pumped backward into the electrochemical flow cell, when the energy is needed again.
During the discharge process, the polarized dispersions are pumped back from these two vessels in the electrochemical cell, in absence of an external bias, where the active materials can be fully discharged to restore the energy. This energy storage mechanism, showed in Figure 5.2, due to the formation of an electric double layer onto the surface of the carbon particles, does not involve redox processes [14].

![Figure 5.2 – Scheme of the formation of the electrical double layer (EDL) onto the surface of carbon particles.](image)

The major challenges in this field include the optimization of the rheological and electrical performances of carbon dispersion, and, consequently, the development of new fluids with low viscosity and high conductivity and capacitance.

In this chapter, several investigations of flowable electrode rheology, shear dependent electrical conductivity, and flow assisted charge and discharge of aqueous carbon dispersions are investigated according to the above objectives.

### 5.2 – Percolation theory

The phenomenon of electrical percolation is fundamental for the electrical conduction of flowable electrodes (FEs) during their flow. The percolation in this case describes the onset of the formation of an infinite cluster of conductive particles suspended in an insulating medium. At the percolation threshold, the system becomes electrically conductive.

In a composite system containing conductive particles, the composite undergoes an insulator-to-conductor transition with typical percolation behavior as the conducting filler content gradually increases. The transition occurs at a particular volume fraction of conductive particles $\phi_c$, known as critical threshold. This behavior is attributed to the
formation of multiple, continuous electron paths, or conducting network, in the matrix of the composite, when the filler content is at or above the percolation threshold.

In Figure 5.3, optical microscope photographs show the morphology of Ketjenblack clusters in Arabic Gum 1.5 wt% and Sodium Alginate 0.5 wt% with (NH₄)₂SO₄ 2 M.

Below the critical concentration $\phi_c$, the carbon dispersion has a very low conductivity; therefore, it can be considered as an insulator.

In this state, clusters of carbon particles are separated from each other, and do not form a conductive pathway. At the percolation threshold, the amount of carbon particles is high enough to form a conductive path through the sample, resulting in an increase of the conductivity of the system. Above the percolation threshold, these clusters grow and cover the entire network because of coalescence.\textsuperscript{[15]}

Mathematical treatment of the phenomenon demonstrated that the percolation threshold depends on particle shape and degree of coordination.
For example, for a 2D percolated system with coordination 4 in a square lattice $\phi_c = 0.59$, whereas for a 3D percolated cubic system with coordination 12, $\phi_c = 0.20$. Near the percolation threshold, the conductivity is defined by the expression:

$$\sigma_e \propto (\phi - \phi_c)^\alpha \quad (5.1)$$

where, $\phi$ is the volume fraction of the particles, $\phi_c$ is the percolation threshold and $\alpha$ is an exponent that depends on the dimensionality of the network $^{[16]}$. Although the percolation phenomenon derives from statistical and geometrical factors, it has been shown that it also depends on chemical-physical factors such as the shape, the aspect ratio of the particles as well as their superficial chemistry, the interactions between particles, surface tension and the methods of preparation of the dispersions.

For example, Geng et al. $^{[17]}$ reported that the use of a surfactant in carbon nanotube dispersions can shift the percolation threshold due to weaker interactions between particles due to the electrostatic barrier formed by the surfactant surrounding the particles. The effect of size and aspect ratio has also been shown in numerous works $^{[18,19]}$.

In this regard, it has been demonstrated that particles with a high aspect ratio are able to form percolation paths at low concentrations $^{[20,21]}$. Indeed, the excluded volume of an anisotropic particle (length $L$, width $r$) is much greater than its actual size; therefore, the volume around the particle in which there is a non-zero probability of contact with another particle is higher.

However, for a 2D planar system, such as graphene-based materials, with high aspect ratio, the isotropic-nematic transition occurs before the percolation threshold $^{[22]}$. It is therefore likely that a 2D carbon material is not suitable as flowable electrode. Concerning the effect of the formulation of the carbon dispersion, Krause et al. $^{[23]}$ reported that the mixing velocity in carbon/polyamide composite affects the electrical conductivity of the system by recounting different percolation threshold values caused by the mixing method.

However, it is worth noting that at the percolation threshold, there is also a dramatic variation of the rheological properties of the system. In fact, the formation of networks and percolation pathways causes an increase of the viscosity.
This observation is of fundamental importance for our purpose, since, as we said earlier, a good flowable electrode must have both high conductivity and low viscosity. Therefore, it is necessary to find the right compromise between the electrical percolation of the system and its viscosity.

5.3 – Results and Discussion

As already discussed above, the rheological and electrical properties of carbon black dispersions determine their efficiency. An ideal carbon dispersion should have a low viscosity to ensure an effective flowability in the cell and to avoid clogging phenomena, while maintaining high capacitive performances. However, obtaining a percolated carbon dispersion with a low viscosity is difficult. Furthermore, these carbon black suspensions must be stable over time in terms of conductivity performances.

In this regard, the choice of the surfactant and stabilizer is critical in obtaining the desired properties. Previous studies have reported formulations of a carbon dispersion stable over time using Arabic Gum as surfactant, and sodium alginate, a polymer in solution that works as stabilizer. The choice of Arabic Gum is due to the high dispersion ability, while sodium alginate prevents sedimentation of carbon particles over time. Moreover, this continuous phase shows a Newtonian viscosity.

Several studies have been focusing on effective ways of reducing the viscosity of flowable electrodes without affecting their capacitive behavior and electrical performance. The viscosity of a carbon flowable electrode depends on the rheological properties of the continuous phase, the interactions between the particles in the continuous phase and the mutual interactions between the two phases. The continuous phase here consists of the aqueous dispersion of the surfactant, the polymer and the electrolyte. The presence of a strong excess of electrolyte is necessary for capacitive energy storage purposes, but it may affect the interactions between the dispersed and continuous phases causing a change in the rheological behavior, usually making it worse. For example, Porada et al. reported that the presence of salt in the dispersing aqueous phase caused an increase in viscosity of a carbon flowable electrode, in particular at lower shear rates.

Unlike many other carbon dispersions described in the literature, however, our carbon dispersion is stabilized by an electrically charged polymer, such as sodium alginate.
This polymer, moreover, allows tuning the rheological properties of the continuous phase, acting on the ionic strength of the solution and/or the pH [29-31].

Variations in ionic strength and pH might have a profound effect on the continuous phase, especially on the polymer chain extension and solution viscosity.

In order to investigate the rheological properties of the continuous phase, different electrolytes have been studied. In this manuscript, we will report only a few cases in which such properties were altered in a substantive manner. To measure the viscosity and the shear stress as a function of the shear rate, an AR1000 controlled stress rheometer (TA instrument) is used. The geometry used is a Plessy glass plate of 60 mm diameter, and the gap fixed at 800 µm. For gaps larger than 500 µm, results do not depend on the gap width, as demonstrated by several studies, not shown in this manuscript. A ramp of shear rate is applied from 500 s\(^{-1}\) to 0.1 s\(^{-1}\), with 10 points per decade.

Each shear rate is maintained for 30 sec and the viscosity is measured by averaging the measurements over the last 5 sec. The temperature is set with a Peltier system at 20°C.

Viscosity behaviors of the continuous phases are presented in details in Fig. 5.4.

![Figure 5.4 - Rheology measurements of the continuous phase made of Arabic Gum 1.5 wt% and Sodium Alginate 0.5 wt% in different electrolytes.](image)

The continuous phase made of Arabic Gum 1.5 wt% and sodium alginate 0.5 wt%, without electrolyte has a Newtonian behavior with viscosity of 0.01 Pa.s. The addition of the KOH 2 M to the dispersion does not affect its Newtonian behavior, but it lowers the viscosity of the system to 0.001 Pa.s, roughly one order of magnitude lower.
By contrast, the addition of NaOH 2M worsens the rheological properties of the system, that, in these conditions, shows a non-Newtonian behavior with a viscosity of 0.05 Pa.s at 10\(^{-1}\) sec\(^{-1}\). Finally, in presence of \((\text{NH}_4)_2\text{SO}_4\) 2 M, the continuous phase shows a Newtonian behavior with a viscosity of 0.005 Pa.s. It is worth noting that in the latter case the ionic strength is higher than for the other two electrolytes. Nevertheless, further studies will be needed in order to understand the effect of the electrolyte on the rheological properties of the continuous phase on a more fundamental level. As a matter of fact, it is known that the conformation of the polymer varies as the electrolyte is added to the solution, as well as its charge density, affecting the polymer-polymer and polymer-surfactant interactions, responsible for the rheological properties of the continuous phase \[^{32}\].

Figure 5.5 – Scheme of the two-compartment configuration electrochemical cell used in cyclic voltammetry measurements. In this configuration, the counter electrode and the reference electrode are short-circuited.
In addition to viscosity, the choice of the electrolyte must not alter the electrical and capacitive properties of the final carbon dispersion. Therefore, the rheological measurements of the continuous phase were combined with cyclic voltammetry measurements in order to monitor potential faradic or pseudo-faradic processes in the voltage range investigated. The electrical measurements have been performed using the electrochemical cell with two-compartment configuration, as shown in Figure 5.5.

These two compartments are separated by an anion exchange membrane, (SnakeSkin® Dialysis Tubing 1000 MWCO). Cyclic voltammetry was performed at a triangular potential between 0 and 1 V at 1 mV/s for each sample.

Figure 5.6 shows the cyclic voltammetry of a test dispersion made of Ketjenblack 7.0 wt% in Arabic Gum 1.5 wt% and Sodium Alginate 0.5 wt% in the same electrolytes used for the rheology tests. Each curve refers to a scan rate of 1 mV/s.

All values for the specific gravimetric capacitance were normalized by the weight of the active carbon material, not the total dispersion mass, to enable a direct comparison with conventional supercapacitor electrodes (which are also normalized to the content of active material). The specific gravimetric capacitance of the slurries was calculated using the equation 5.2

\[ C_{sp} = \frac{2i}{m \cdot (\frac{dv}{dt})} \]  

where, \( i \) is the value of measured current in the cyclic voltammetry and \( \frac{dv}{dt} \) is the scan rate, as shown in Figure 5.6.

The continuous phase in the absence of electrolyte (black line) shows a cyclic voltammetry profile, which does not show the typical rectangular shape typical of the capacitive charge storage due to electric double layer formation or electrosorption of ions. Instead, it is possible to observe a resistive behavior due to the absence of charged species in strong excess in solution. The specific gravimetric capacitance is 14 F/g. The addition of NaOH 2 M shows a substantial improvement in the electrical performances, characterized by the typical
rectangular shape of a classic EDL (Electric Double Layer), with a specific gravimetric capacitance value of 60 F/g.

On the other hand, the addition in dispersion of KOH 2 M, worsens the electrical performances, with the appearance of pseudo-faradic processes, and reduced the capacitive current of the system. Finally, the addition of (NH₄)₂SO₄ does not induce faradic processes in the potential range applied and improves the capacitive current with a specific gravimetric capacitance of 20 F/g.

![Cyclic voltammograms and relative specific capacitance](image)

Figure 5.6 - Cyclic voltammograms and relative specific capacitance of Ketjenblack dispersion 7.0 wt% in Arabic Gum 1.5 wt% and Sodium Alginate 0.5 wt% in different electrolytes.

Considering the above results, the electrolyte chosen for our purposes is therefore the (NH₄)₂SO₄, since it slightly improves the rheological properties of the continuous phase, and its electrical properties as well.

### 5.3.1 – Measurement of electronic conductivity

In order to determine the electrical percolation threshold, DC chronoamperometry measurements have been performed at different concentrations of carbon in the dispersion. The experimental difficulty of this measure lies in the fact that the electronic conductivity must not be confused with the ionic conductivity. The latter is not negligible due to the presence of a strong excess of electrolyte in solution and numerous charged species due to the dissolved polymers (Sodium Alginate and Arabic Gum).
Therefore, to determine only the contribution of the electronic conductivity, the measurement must be performed at "zero frequency" conditions. To this end, the measurement needs a certain amount of time in order to avoid the electrodes polarization currents due to the mobility of the free charges in solution. The measurements are carried out with a two-plate capacitor cell connected to a potentiostat/galvanostat (Metrohm Autolab/PGSTAT101). The platinum electrodes of this cell are symmetrical with a square surface $A=3 \text{ mm} \times 3 \text{ mm}$ and separated by a distance $d=3 \text{ mm}$. The cell probe is immersed in the carbon dispersion over a height of 1.5 cm, as shown in Figure 5.7. A voltage of +1 V is applied to the electrodes and the current is measured for a long period of time (2000 sec) until the polarization currents are stabilized. This measured $I_{\text{plateau}}$ current allows us to calculate the electrical resistance between the two electrodes and the electronic conductivity knowing the cell geometry by using the expression:

$$\sigma_e = \frac{I_{\text{plateau}}}{|E|} \cdot \frac{d}{A} \quad (5.3)$$

where $I_{\text{plateau}}$ is the stabilized current measured at 2000 seconds, $|E|$ is the applied voltage in modulus, $d$ is the distance between the electrodes and $A$ is the surface area of the electrodes. However, it should be noted that it is difficult to measure electronic conductivities lower than 0.01 mS/cm with this method.

This is due to a residual ionic conductivity that is impossible to avoid, even after long stabilization. Therefore, it will be considered that the dispersion has a non-negligible electronic conductivity only when its conductivity is higher than this value.

Figure 5.8 shows the electronic conductivity results for two different aqueous carbon dispersions which display a different percolation behavior.

At low carbon percentage values, the dispersions are not electrically conductive since their conductivity is about 0.01 mS/cm.

As the concentration of conductive particles increases, there is a substantial increase in electronic conductivity. In particular, in Figure 5.8, it is possible to observe how the Ketjenblack conductivity curve displays an S-shape with a percolation threshold around 6
wt%, whereas for the Acetyleneblack dispersion, the electronic conductivity becomes significant at concentrations of 4 wt% but it does not show a clear S-shape percolation curve. Previous studies have already shown that these two different percolation behaviors are due to different morphologies of the clusters \[24\]. The clusters of Acetyleneblack are more filamentous and display a fractal-like shape, whereas the Ketjenblack show dense and compact clusters. Open fractal clusters of Acetyleneblack are associated to a lower percolation threshold. As the clusters are open and deformable, the viscosity at percolation is also low.

![Figure 5.7 – DC Chronoamperometry measurements of electronic conductivity of the carbon dispersions. The current values related to the electronic conductivity are the stabilized values at the plateau. A square voltage of +1 V is applied to the electrode for 2000 seconds in order to avoid the polarization currents due to the presence of free charges in the system.](image)

Above percolation, the clusters entangle to form a more compact network. This induces a more continuous increase of the conductivity and of the viscosity above percolation. By contrast, dense clusters of Ketjenblack do not allow any flexibility of the carbon network once percolated, and therefore the properties vary only slightly above percolation \[26\]. The structure difference between these two different CB particles arises from the dynamics formation of the particle clusters.
In Acetylenblack, the fractal clusters reflect an aggregation mechanism limited by diffusion (Diffusion limited aggregation DLA). Such a mechanism takes place when there only a weak repulsive barrier, between the particles.

By contrast, the dense clusters of Ketjenblack, shows a higher repulsive barrier between them reflecting an aggregation limited by reaction (RLA). The origin of these interactions involves the surface chemistry of the particles and the adsorption kinetics and efficiency of the polymeric surfactants \[33\].

The progressive increase of the electronic conductivity and the moderate viscosity of its dispersions makes Acetyleneblack a particularly suitable material for the implementation in flowable electrodes \[26\].

Figure 5.8 – Electronic conductivity of dispersion of Ketjenblack and Acetylene black in Arabic Gum 1.5 t% and Sodium Alginate 0.5 wt% in \((\text{NH}_4)_2\text{SO}_4\) 2 M based on the filler content of carbon (wt%). (Error bar correspond to the standard deviation).
Nevertheless, we choose to focus on the Ketjenblack because, unlike Acetyleneblack, it has a high porosity, which is an advantage for capacitive energy storage. More detailed characteristics of the two kind of carbon black are given in Table 5.1.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Density of the powder (g/L)</th>
<th>BET surface area (m²/g)</th>
<th>DBP absorption (cm²/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ketjenblack</td>
<td>AkzoNobel 100-120</td>
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<td>495</td>
</tr>
<tr>
<td>Acetyleneblack</td>
<td>Alfa Aesar 80-120</td>
<td>80</td>
<td>200-250</td>
</tr>
</tbody>
</table>

Table 5.1 - Brief summary of some critical properties of each Carbon black.

### 5.3.2 – Rheology measurement of flowable electrodes

The rheological behavior of the samples is presented in more details in Figure 5.9, where the shear stress and viscosity are plotted as a function of the shear rate from 0.1 to 500 s⁻¹. As previously mentioned, the continuous phase made of Sodium Alginate 1.5 wt% and Arabic Gum 0.5 wt% in (NH₄)₂SO₄ 2 M has a Newtonian viscosity of 0.005 Pa.s. The addition of carbon particles increases the viscosity and the final dispersion exhibits a shear-thinning behavior with viscosity values lower than 100 Pa.s at low shear rate, for carbon black concentrations up to 7.0 wt%. Although these viscosity and shear stress values are high enough for common fluid electrodes reported in the literature, the dispersion we formulated at 7.0 wt% in carbon particles is compatible to flow into our test set-up without showing any phenomena of occlusion.

A Herschel-Bulkley model for yield stress fluid can be applied to fit the rheology curves using the equation (5.4).

\[
\sigma(z) = \sigma_0 + \xi \dot{\gamma}(z)^\beta
\]

(5.4)

where, \(\sigma(z)\) is shear stress, \(\sigma_0\) is the yield stress, \(\dot{\gamma}(z)\) shear rate and \(\xi\) and \(\beta\) are parameters deduced from the fitting of the experimental rheological curves.
Figure 5.9 - Rheology measurements of the Ketjenblack dispersion in Arabic Gum 1.5 wt% - Sodium Alginate 0.5 wt% in (NH₄)₂SO₄ 2 M. Several percentages of carbon are presented. Shear stress curves have been fitted using the Herschel-Bulkley law.

Even for a small addition of carbon black particles, the final suspensions show yield stress phenomena. These results suggest the formation of a network by the dispersed particles. In Table 5.2 the parameters obtained from the Herschel-Buckley fit are reported.

<table>
<thead>
<tr>
<th></th>
<th>Reference</th>
<th>3.0 wt%</th>
<th>5.0 wt%</th>
<th>7.0 wt%</th>
<th>9.0 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_0$</td>
<td>9.97e-4</td>
<td>0.059</td>
<td>0.74</td>
<td>7.18</td>
<td>194.50</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>0.0503</td>
<td>0.014</td>
<td>0.17</td>
<td>1.25</td>
<td>8.56</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1.000</td>
<td>0.86</td>
<td>0.71</td>
<td>0.68</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Table 5.2 - Brief summary of some critical properties of each Carbon black

### 5.3.3 - Electric measurement under shear

As previously mentioned, in a conventional solid-state carbon electrode, the charged species are free to diffuse into the microstructure of the porous material. In recent years, several studies have been devoted to better understand the dynamics of the migration of the charged species from and into the material to enhance the capacitive properties. In a flowable electrode, on the other hand, the electric properties must be studied under the effect of the shear stress to verify how they vary in dynamic conditions \cite{34,35}.

In this regard, a detailed study of the laminar flow in a tube of these carbon dispersions has been carried out \cite{24-26}. 

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Since the flow rate is geometry-dependent, the most useful parameter for these studies is the shear stress at the wall of the channel. The conversion from flow rate to shear stress is done by using a model of the laminar flow inside two plates channel, where the velocity gradient is distributed along the length of the channel (\(\vec{x}\)), and it varies only along the height direction (\(\vec{z}\)). The rectangular geometry of the channel used in our flow dependent measurements, matches with the geometry described in the hypothesis of the model, since the width of the channel of the electrochemical cell (\(w = 0.8\) cm) is much larger than its thickness (\(e = 0.3\) cm), and it has a length of (\(L = 1\) cm).

Under these assumptions, the drop of pressure \(\Delta P = P_{in} - P_{out} > 0\) between the inlet and the outlet, the shear stress \(\sigma(z)\), the shear rate \(\dot{\gamma}(z)\) and the velocity profile \(v(z)\) are linked by the following relations:

\[
\sigma(z) = \frac{\Delta P_z}{L} \quad \text{and} \quad \dot{\gamma}(z) = \frac{dv(z)}{dz} \tag{5.5}
\]

where, \(z\) is the coordinate along the height direction (\(\vec{z}\)), and it is equal to zero in the middle of the channel. To calculate the velocity gradient, we fit the flow curve that correlates the shear rate \(\dot{\gamma}(z)\) and the shear stress \(\sigma(z)\) with the Herschel-Bulkley equation:

\[
\sigma(z) = \sigma_0 + \xi \dot{\gamma}(z)^\beta \tag{5.6}
\]

which can be expressed through the formula 5.5, obtaining:

\[
\frac{\Delta P_z}{L} = \sigma_0 + \xi \left(\frac{dv}{dz}\right)^\beta \tag{5.7}
\]

where, \(\sigma_0\) is the yield stress and \(\xi\) and \(\beta\) are parameters deduced from the fitting of the experimental rheological curves reported in the previous paragraph.
After calculations, we obtain the velocity gradient profile \( \overline{v}'(z) \). This gradient is valid for \( z \geq 0 \), but for \( z \leq 0 \), it is necessary to change the sign of \( z \) because the profile is symmetric with respect to \( z = 0 \). Therefore, by rearranging the equation (5.7) we obtain:

\[
\frac{dv(z)}{dz} = \frac{L \xi \beta}{(\beta + 1) \Delta P} \left( \frac{\Delta P_z}{L} - \frac{\sigma_0}{\xi} \right)^{\frac{1}{\beta}}
\]

which after integration is expressed by:

\[
v(z) = \frac{L \xi \beta}{(\beta + 1) \Delta P} \left( \frac{\Delta P_z}{2L} - \frac{\sigma_0}{\xi} \right)^{\frac{\beta+1}{\beta}} + \text{constant}
\]

The expression can only be solved if \( \frac{\Delta P_z}{2L} - \frac{\sigma_0}{\xi} \geq 0 \), where \( z \geq \frac{L \sigma_0}{\Delta P} \). This value \( z = \frac{L \sigma_0}{\Delta P} \), represents the limit between the area near the wall of the channel, where the shear stress has a higher impact and the area of the center of the channel at constant velocity. Given the
roughness of the carbon paper electrodes (around 20 μm), we can safely assume a no-slip condition at the boundaries, \( u(e/2) = 0 \), obtaining:

\[
    u(z) = \frac{L \xi \beta}{(\beta + 1) \Delta P} \left[ \left( \frac{\Delta P}{2L} - \frac{\sigma_0}{\xi} \right)^{\frac{\beta+1}{\beta}} - \left( \frac{\Delta P_z}{2L} - \frac{\sigma_0}{\xi} \right)^{\frac{\beta+1}{\beta}} \right]
\] (5.10)

In the middle of the channel, the fluid flows with a constant velocity, as evident from top front profile in Figure 5.10. The same calculation for the negative \( z \) gives the following velocity profile \( \vec{u}(x) \) in the channel.

These equations describe the flowing of the carbon dispersions close to the walls of the channel (for \( z \geq \frac{L \sigma_0}{\Delta P} \)), characterized by a high shear-stress. On the other hand, the shear-stress is not strong enough at the center.

\[
    \ddot{u}(z) = \begin{cases} 
        \frac{L \xi \beta}{(\beta + 1) \Delta P} \left[ \left( \frac{\Delta P}{2L} - \frac{\sigma_0}{\xi} \right)^{\frac{\beta+1}{\beta}} - \left( \frac{\Delta P_z}{2L} - \frac{\sigma_0}{\xi} \right)^{\frac{\beta+1}{\beta}} \right] & \text{for } \frac{L \sigma_0}{\Delta P} \leq z \leq \frac{e}{2} \\
        \frac{e \xi \beta}{(\beta + 1) \Delta P} \left( \frac{\Delta P}{2L} - \frac{\sigma_0}{\xi} \right)^{\frac{\beta+1}{\beta}} - \left( \frac{\Delta P_z}{2L} - \frac{\sigma_0}{\xi} \right)^{\frac{\beta+1}{\beta}} & \text{for } \frac{L \sigma_0}{\Delta P} \leq z \leq \frac{L \sigma_0}{\Delta P} \\
        \frac{L \xi \beta}{(\beta + 1) \Delta P} \left[ \left( \frac{\Delta P}{2L} - \frac{\sigma_0}{\xi} \right)^{\frac{\beta+1}{\beta}} - \left( \frac{\Delta P_z}{2L} - \frac{\sigma_0}{\xi} \right)^{\frac{\beta+1}{\beta}} \right] & \text{for } \frac{e}{2} \leq z \leq -\frac{L \sigma_0}{\Delta P} 
    \end{cases}
\]

After integration of \( \ddot{u}(z) \) on the whole surface of the channel, a relationship is found between the flow rate \( Q \) and the pressure difference \( \Delta P \):

\[
    Q = \frac{eL \xi \beta w}{(\beta + 1) \Delta P} \left( \frac{\Delta P}{2L} - \frac{\sigma_0}{\xi} \right)^{\frac{\beta+1}{\beta}} - \frac{2w (L \xi \beta)^2}{(2 \beta + 1) (\beta + 1) \Delta P^2} \left( \frac{\Delta P}{2L} - \frac{\sigma_0}{\xi} \right)^{\frac{\beta+1}{\beta}}
\] (5.11)
By using this relationship, the flow rate \( Q \) in (mL/min) can be finally converted into pressure difference \( \Delta P \) (Pa). Then, the shear stress at the wall and the corresponding shear-rate for a given dispersion is found at \( z = \pm e/2 \) replacing the pressure difference in expression 1:

\[
\sigma_w = \frac{\Delta P e}{2L} \quad \text{and} \quad \gamma = \left( \frac{\sigma_w - \sigma_0}{\xi \beta} \right)^{\frac{1}{\beta}}
\] (5.12)

Through this procedure it is possible to calculate the shear stress and the corresponding shear rate of a sample with known viscosity for a given geometry as shown in Figure 5.11. Moreover, the correlation of these two basic parameters of the flow is in agreement with the rheological measurements performed with a classical rheometer shown in the previous paragraph. AC electrical measurements under shear flow have been performed using a specific setup and the classic correction protocol explained in chapter II. Figure 5.12 shows the effect of the shear rate on the electrical conductivity of the sample under study. In particular, the graph shows the trend of the normalized conductivity (calculated as the ratio of the dynamic measurement to the static one) against the shear rate.

![Figure 5.11 – Correlation between the flow-rate and correspondent shear stress at wall and shear rate for a given geometry (w=0.8 cm, e=0.3 cm and L=1 cm) and a specific carbon dispersion made of Ketjenblack 7.0 wt% in Arabic Gum 1.5 wt% - Sodium Alginate 0.5 wt% in (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} 2 M with (\( \xi = 1.25 \), \( \sigma_0 = 7.18 \), and \( \beta = 0.68 \)).](image)

It is possible to observe how this trend does not involve significant variations in conductivity, which is almost constant for every shear rate. These results suggest that the flow does not alter the structure of the percolated carbon dispersion. The choice of a concentration above
the percolation threshold guarantees the presence of percolation network paths for the charge, even in dynamic conditions. This result is encouraging for our purpose to use the slurries as flowable electrodes.

Figure 5.12 – Electro-rheological behavior of a Ketjenblack 7.0 wt% dispersion in Arabic Gum 1.5 wt% - Sodium Alginate 0.5 wt% in (NH₄)₂SO₄ 2 M. In figure is shown the value of normalized electronic conductivity in the frequency range of interest.

### 5.3.4 – Electrical characterization of flowable electrode

For the electrochemical characterization, the carbon flowable dispersion was tested in a two-electrodes symmetric configuration, as show in Figure 5.5. Each flowable electrodes were volumetrically similar and were separated from each other using an anion exchange membranes. The electrochemical performance of the flowable electrodes was studied using cyclic voltammetry with a potentiostat/galvanostat (Autolab PGSTAT204 Metrohm).

Figure 5.13 (A) shows the cyclic voltammetry of the carbon dispersion under study at different scan rates. In details, the electric behavior of the sample does not show a typical rectangular shape characteristic of a formation of electric double layer. The distortion of the CV curves suggests that there is a large resistance $R_{Leakage}$.

This resistance can be generated by different factors such as, the intimate contact of the dispersions with the current collectors for the injection and extraction of the charge, and the contact resistance between the particles $^{[36]}$.

Further studies are needed to better understand the reason of these limitations and their negative contribution to the electrical performance of the carbon dispersion. Figure 5.13 (B)
shows the specific gravimetric capacitance of the sample calculated using the equation 5.2. In details, it possible to observe how this feature is rate-dependent and show highest specific gravimetric capacitance at low scan-rate. In particular a specific capacitance of 20 F/g is calculated at 1 mV/s. The influence of scan rate presumably originates presumably from a porosity with a broad range of characteristic sizes.

Figure 5.13 - Cyclic voltammograms and relative specific gravimetric capacitance of Ketjenblack dispersion 7.0 wt% in Arabic Gum 1.5 wt% and Sodium Alginate 0.5 wt% in (NH₄)₂SO₄ 2 M.

The smallest pores are less accessible than bigger ones. At fast scan rate, it is likely that the small pores does not contribute to the storing of charges, resulting in a lower effective capacitance.

Figure 5.14 - Specific gravimetric capacitance against scan rate
5.3.5 – Self-Discharge

The self-discharge of the system is an important phenomenon to take into account for any energy storage technology. The entity and speed of the self-discharge, in fact, play a critical role in determining the potential applications of these systems [37-40]. However, this undesirable phenomenon is inevitable; therefore, it is of crucial importance to quantify the energy loss due to self-discharge and to identify strategies to reduce it [41,42]. In conventional supercapacitors, this phenomenon, perceived as a decrease of the cell voltage, occurs in open-circuit conditions.

Figure 5.15 – Open circuit voltage measurements of a 5.0 g of Ketjenblack dispersion 7.0 wt% in Arabic Gum 1.5 wt% - Sodium Alginate 0.5 wt% in 2M (NH4)2SO4.
The decrease of the cell voltage is mainly due to two reasons: charge dissipation and ions redistribution. During charge dissipation, the adsorbed charges are released from the surface of the carbon particle, causing a decrease in the voltage and in the recoverable charge. During the ions redistribution, the adsorbed charges are redistributed on the surface of the carbon particles, decreasing the intensity of the electric double layer. Moreover, they may participate in undesirable redox process, which also produce a decrease in the cell voltage. The charge dissipation occurs along the RC circuit and the connections with the electrical set-up, while the ions redistribution occurs in the active material.

To measure the entity of the self-discharge in the carbon dispersion under examination, several open circuit measurements were performed. In detail, two self-discharge curves were compared for two different charging times.

Once the electrochemical cell is filled with 5.0 g of active material (Ketjenblack 7.0 wt% in Arabic Gum 1.5 wt% - Sodium Alginate 0.5 wt% in 2M (NH₄)₂SO₄), the latter is subjected to a charging process at 1V for 500 seconds or 20 minutes. At the end of the charging process, the RC circuit is opened, in order to electrically insulate the supercapacitor, which remains connected only to the oscilloscope. This should exclude any discharge processes due to dissipation along the circuit shunts. This operation allows us to measure only the charge redistribution processes within the active material. Figure 5.15 shows the self-discharge curves corresponding to the two charge processes. After 10000 sec, the system shows a charge decrease of 20% when the charging process is only 500 seconds while the decrease is of 10% when the charge process is 20 minutes long.

5.3.6 – Flow assisted Charge and Discharge

In order to verify the ability of this flowable electrode to transport and store charges in electrochemical flow capacitor technology, flow assisted charge and discharge processes were performed. Firstly, we will focus on the charge process of a conventional supercapacitor in static condition in a RC circuit. This process is expressed by the equation shown below:
\[ V_{\text{out}}(t) = V_{\text{in}} \left( 1 - e^{-\frac{t}{R_cC}} \right) \]  \hspace{1cm} (5.13)

where, \( V_{\text{out}}(t) \) is the potential across the supercapacitor at time \( t \), \( V_{\text{in}} \) is the potential supply to the circuit, \( t \) is the elapsed time since the application of the supply voltage, \( R_c \) is the resistance value during the charge process and the product \( R_cC \) is the time constant of the \( R_cC \) charging circuit, also denoted as \( \tau \).

As consequence, the discharge process is governed by the same parameters according to the expression:

\[ V_{\text{out}}(t) = V_{\text{out}} e^{-\frac{t}{R_dC}} \]  \hspace{1cm} (5.14)

where, \( V_{\text{out}} \) is the final potential of the charged supercapacitor and \( R_d \) is the resistance value during the discharge process. Figure 5.16 (A) show the charge and discharge processes of a supercapacitor in static conditions.

In detail, the area defined by integral of the difference between the voltages supply to the circuit and the voltage across the supercapacitor represent the amount of charge stored in the system, as show in equation 5.15.

\[ \int \frac{V_{\text{in}} - V_{\text{out}}}{R} dt = \int \frac{V_R}{R} dt = \int i dt = Q \]  \hspace{1cm} (5.15)

These considerations made for the static conditions are also valid in the presence of the flowing electrodes. The dynamic nature of these processes results in differences from the usual behaviors of charge and discharge processes. During the charge process, the introduction of the new uncharged dispersion into the electrochemical cell, leads to a leak of current and to a decrease of the voltage across the cell below the expected values.

Conversely, during the discharge process, the reintroduction of charged carbon dispersions, in the active area of the electrochemical cell, leads to an increase of the voltage across the cell above the expected values. The dynamic nature of these processes allows the storage and conversion of a larger amount of charges as shown in figure 5.16 (B).
In order to verify the ability of our carbon dispersion to act as a flowable electrode a simple experimental setup has been designed to test its validity. The two-compartment electrochemical cell was connected by means of silicone tubes to 4 syringes. The latter, will act as the vessels of the system for the uncharged and charged dispersions. This electrochemical cell is connected to a RC circuit which is directly connected to a waveform generator (Trueform 33500B, Keysight). The charging process is performed at 1 V for 200 seconds by using a resistance of 178 Ω. In this phase, the uncharged carbon dispersion is pumped by syringe-pumps through the electrochemical cell, where the electric field charges the slurries. The charged slurries are collected in the other two syringes. During the discharge process, the circuit is short-circuited by means of a switch. This procedure allows us to perform voltage measurements related only to the decoupling of the electric double layer without other influences. The voltage across the supercapacitor was recorded by means of an oscilloscope (Tektronix DPO 2022B) as shown in Figure 5.14.

Figure 5.14 show the charge and discharge processes of the formulated carbon flowable electrode. As previously mentioned, the effect of the flow alters the voltage values across the cell. In details, in Figure 5.15, are shown only the voltage across the cell in static and in dynamic conditions. All the curves are referred to the formulated carbon dispersion made of Ketjenblack 7.0 wt% in Arabic gum 1.5 wt% - sodium alginate 0.5 wt% in in (NH₄)₂SO₄ 2 M.
The black curve represents the profile of charge and discharge of the dispersion in static conditions.

As shown in Figure 5.13 at $t_1 = 200 \text{ sec}$ the voltage across the cell reaches the value of 0.86 V to discharge completely at $t_2 = 400 \text{ sec}$. At a flow rate of 1 mL/min (red curve), the effect of flow keeps the voltage across the cell constant at a lower value. At time, $t_1 = 200 \text{ sec}$ the process of discharge of the particles begins. During this process in dynamic conditions, the voltage reaches a value greater than the expected value in static. Similar trends were found for other flow rates studied up to 9 mL/min.

Table 5.3 shows the final charge and discharge values of the flowable electrode. These experimental evidences represent a proof of concept of the use of flowable electrodes in the electrochemical flow capacitors. From such charge-discharge measurements it is possible to calculate the stored charge within the system and analyze the effect of the flow using equation 5.15.
Figure 5.15 – Charge and discharge processes of a carbon flowable electrode made of Ketjenblack dispersion 7.0 wt% in Arabic Gum 1.5 wt%, Sodium Alginate 0.5 wt% in (NH₄)₂SO₄ 2 M at different flow rates.

<table>
<thead>
<tr>
<th></th>
<th>Static</th>
<th>1 mL/min</th>
<th>3 mL/min</th>
<th>5 mL/min</th>
<th>7 mL/min</th>
<th>9 mL/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>t₂ = 200 sec</td>
<td>0.86 V</td>
<td>0.81 V</td>
<td>0.78 V</td>
<td>0.74 V</td>
<td>0.72 V</td>
<td>0.67 V</td>
</tr>
<tr>
<td>t₂ = 400 sec</td>
<td>0 V</td>
<td>0.0053 V</td>
<td>0.014 V</td>
<td>0.018 V</td>
<td>0.035 V</td>
<td>0.053 V</td>
</tr>
</tbody>
</table>

Table 5.3 – Voltage across the cell in charge and discharge at time t₁ and t₂.

Figure 5.16 – Stored and converted charge profiles during the charge-discharge processes of the electrochemical flow capacitor at different flow rates.

The stored charge evolution, expressed in coulomb, during the charge and discharge processes of the supercapacitor are shown in Figure 5.16. At time t₁ = 200 sec the amount
of charge is equal to 0.19 C. The effect of flow results in an increase of stored charges both
during the charging process and during the discharge process, where the progressive
replacement of charged dispersion maintains the amount of charge higher than the static
conditions. More details on the charge values during the two processes are shown in Table
5.4.

<table>
<thead>
<tr>
<th></th>
<th>Static</th>
<th>1 mL/min</th>
<th>3 mL/min</th>
<th>5 mL/min</th>
<th>7 mL/min</th>
<th>9 mL/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_1 = 200 \text{ sec}$</td>
<td>0.19 C</td>
<td>0.23 C</td>
<td>0.26 C</td>
<td>0.28 C</td>
<td>0.31 C</td>
<td>0.37 C</td>
</tr>
<tr>
<td>$t_2 = 400 \text{ sec}$</td>
<td>0.13 C</td>
<td>0.14 C</td>
<td>0.15 C</td>
<td>0.16 C</td>
<td>0.17 C</td>
<td>0.20 C</td>
</tr>
</tbody>
</table>

Table 5.4 – Stored and converted charges in C values during the two processes values at time $t_1$ e $t_2$

From these considerations, it is possible to carry out a more detailed analysis of the effect of
the flow on the charge and discharge processes of the carbon flowable electrode. Figure
5.17 (A) show the evolution of the normalized maximum charge stored at time $t_1 = 200 \text{ sec}$
against the flow rate. In particular, we can observe how at low flow rate values, where the
active area of the electrochemical cell is crossed by a lower quantity of carbon dispersion,
this succeeds in storing a greater quantity of charges per amount of materials.

![Figure 5.17](image)

Figure 5.17 – Effect of the flow on the stored charge in dynamic conditions.

By contrast, as the flow rate increases, a greater amount of dispersion travels through the
active area of the electrochemical cell with the effect of a lower amount of charge stored per
carbon particles.
The value of maximum charge acquired by the system in relation of the flow rate in showed in Figure 5.17 (B). The amount of charge grows linearly with the flow. Presumably, this trend is characterized by a linear regime at low flow rates, which should saturate at high flow rates, not reached in the present experiments.

5.4 – Discussion and comparison with literature

As mentioned in the introduction, the major challenges in this field include the optimization of the rheological and electrical performances of carbon dispersions, and, consequently, the development of new fluids with low viscosity and high conductivity and capacitance. In this chapter, we presented the potential use of an aqueous carbon dispersion, based on Ketjenblack carbon particles, capable of flowing in micro-channel (3 mm) and showing a very high electronic conductivity (2 Pa.s at 5 sec\(^{-1}\) and 65 mS/cm for a concentration of 7.0 wt%). Moreover, these dispersions show a high stability over several months due to the specific formulation of the continuous phase, due to the presence of a polyelectrolyte, which prevents the sedimentation of the carbon particles without altering the rheological properties of the system. Making a direct comparison between the results presented in this work and the data in the literature is not easy to interpret because of the different methodologies and materials presented in the literature. In particular, it is difficult to compare such values between pure carbon dispersions in electrolyte solution and semi-solid electrodes \[^{[34]}\] systems in which carbon powders are used as an added conductive additive. However below, are reported some results present in literature for aqueous carbon flowable electrodes. A direct comparison between electronic conductivity values of different aqueous flowable carbon electrodes of the literature is shown in figure 5.18. It shows the conductivity values against the amount of carbon material presented in weight percent. The amounts of active material, considered as dispersion of carbon particles, varies in a wide concentration range. In particular, Li et al. \[^{[43]}\], have reported values of conductivity for a dispersion of ketjenblack 4.0 wt%, used in semi solid flow cell (SSFC), equal to 5 mS/cm. Subsequently, other values with higher concentration are reported, among which: Paroda et al \[^{[27]}\], with a conductivity of 14 mS/cm, Dannison et al. \[^{[44]}\] and Hatzell et al. \[^{[36]}\] of only 0.01 mS cm and 0.3 mS/cm.
Finally, we report the other two conductivity values, both relating to a dispersion of Ketjenblack 7.0 wt% in the same continuous phase. The only difference in these two dispersions is the presence of the electrolyte in strong excess present in our result. In particular, we report the value shown by Parant et al.\textsuperscript{[26]} equal to 0.1 mS/cm and our result of 65 mS/cm. From these results, it is evident that the presence of an electrolyte in solution, which alters the ionic strength of the dispersion, involves a different arrangement of the dispersed particles. Further studies should confirm the significant difference between these two results or clarify whether the different preparation protocol results in a substantial difference in the percolation threshold as proposed by Krause et al.\textsuperscript{[23]}.

Regarding the comparison of our results of viscosity with the results present in literature, we report, in Figure 5.19, different values of viscosity at 5 sec\textsuperscript{-1} given in different works. Paroda et al.\textsuperscript{[27]} shown a viscosity for a carbon concentration of 15 wt% equal to 8 Pa.s, while Presser et al.\textsuperscript{[6]} of only 2 Pa.s for a concentration of 10 wt%. Hatzell et al.\textsuperscript{[36]} have reported a viscosity value of 10 Pa.s related to a concentration of 20 wt%.
Successively we report the values shown by Campos et al. [11] in which flowable carbon dispersions present a viscosity value of 12 Pa.s for a concentration of 23 wt% of active carbon material. Finally, we report the values by Parant et al. [26] and our result, which corresponds the viscosity values of 9 Pa.s and 2.5 Pa.s for a Ketjenblack dispersion of 7.0 wt%. As already discussed in the previous paragraphs, the difference of this result lies in the choice of electrolyte, which plays a fundamental role in the rheology of the continuous phase.

Finally, we present in figure 5.20, the last basic parameter for flowable electrodes, which is the specific gravimetric capacitance. It should be remembered that this quantity could also be expressed in specific volumetric capacitance, which would allow a direct comparison between the carbon dispersions for a given volume. In particular, Hatzell et al. [36] reported a value of specific gravimetric capacitance of 60 F/g, while Dennison et al. [44], reported 150 F/g. It should be noted that this parameter depends solely on the ability to form a double electrical layer on the surface of the active material. This phenomenon is therefore governed by different factors, such as the porosity and by the surface chemistry of the particles.
Figure 5.20 – Direct comparison of the specific gravimetric capacitance of different works present in the literature and our result in relation to the amount of active carbon material present in the dispersion.

Successively we report the values presented by Boota at al. $^{[13]}$, which showed specific gravimetric capacitance of 100 F/g while Campos et al. $^{[11]}$ reported values of 60 F/g. Finally, we present the value of our dispersion equal to only 20 F/g.

5.5 – Conclusion

The overall objective of this chapter was focused on the study and implementation of a carbon flowable electrode for capacitive energy storage in electrochemical flow capacitor technology. From previous studies it was preferred to use an aqueous dispersion of carbon materials in the presence of Arabic Gum as surfactant and Sodium Alginate as stabilizer. Different tests were performed in order to improve the rheological and electrical performances of these carbon dispersions by using the appropriate electrolyte. The choice to use Ammonium Sulfate 2 M in solution has been adopted as it has improved both rheological and electric properties of the dispersion.

This formulation allowed us to create a percolated flowable carbon electrode by dispersion of Ketjenblack carbon powder in the continuous phase with high electronic conductivity of 65 mS/cm, 3 orders of magnitude higher than the flowable carbon dispersion proposed in
the literature. The formulated dispersion shows still high viscosity, but lower than most values reported in the literature for related materials. Specific gravimetric capacitance of 20 F/g were reported which are still relatively low compared to several works proposed in the literature but compatible for aqueous dispersions. Self-discharge measurements have demonstrated the possible storing of the charge in the formation of an electric double layer on the surface of the particles which can be recovered with certain efficiency in a considerable period of time. Flow-assisted charge and discharge have demonstrated the feasibility of this technology showing a clear charge recovery during the discharge phase. Overall, the progresses made for the conductivity and viscosity would allow a faster charging of the electrode and easier circulation. Future work should be focused on improving the capacitance, using for example more porous carbon black, to make the present formulations really superior to flowable electrodes reported so far.
Reference


Résumé : L'objectif de ce travail est de développer et d'étudier une nouvelle classe de fluides intelligents à base de dispersions colloïdales de carbone, sensibles à un stimulus externe pour des applications de conversion et stockage d’énergie. Ces stimuli sont de différentes natures : vibration mécanique, mouvement humain, variation de pression ou écoulement d’un solvant, et peuvent altérer les structures de tels systèmes. Ceci induit une modification de la structure locale des particules et par conséquent des propriétés diélectriques et électriques. Habituellement, les suspensions de matériaux carbonés sont étudiées au repos ou séchées. Toutefois, comprendre leur comportement en flux est essentiel pour de nouvelles applications où ces matériaux sont exploités dans des conditions dynamiques telle que le stockage d’énergie électrochimique assisté par flux (FAES). Par exemple, les matériaux à base de graphène jouent désormais un rôle important dans les nouvelles technologies énergétiques. Ils sont utilisés comme additifs conducteurs dans les assemblages d’électrodes, mais en raison de leur forme anisotrope spécifique, ils permettent également d’obtenir des fluides diélectriques sous écoulement.

Les cristaux liquides d’oxyde de graphène, en tant que matériau souple électrostrictif, sont étudiés pour la récupération d’énergie mécanique, ainsi que des dispersions de noir de carbone pour le stockage d’énergie.

Les propriétés diélectriques et électriques de ces dispersions fluides dans des conditions statiques et dynamiques sont mesurées et analysées. Enfin, l’effet de l’écoulement sur l’orientation et la réorganisation locale des particules et leur comportement diélectrique et électrique sont examinés.

Mots clés : [Oxyde de Graphène, Spectroscopie Diélectrique, Permittivité, Constante Diélectrique, Cristaux Liquides, Noir de Carbone, Électrodes de Carbone Fluides Percolées, Stockage d’Énergie Électrochimique à Flux Assisté, Supercapacité en Flux]

Abstract : The aim of this work is to develop and study a new class of smart fluids made of colloidal carbon-based dispersions, which are sensitive to an external stimulus for energy storage or conversion applications. The effect of an external input, such as mechanical vibration, human motion, variable pressure, flowing of a solvent, can alter the structures of such systems. Consequently these changes induce modifications of the dielectric and electrical properties. Usually, the suspensions of carbon materials are investigated at rest or dried. However, their flow behavior is critical when new technologies, which exploit these materials in dynamic conditions such as FAES (Flow-Assisted Electrochemical Energy Storage) are considered. For example, graphene-based materials are now playing a significant role in energy materials. They act as conductive additives in electrode assemblies, but due to their specific anisotropic shape they also provide a new route to achieve dielectric liquid media.

In details, Graphene Oxide liquid crystals as electrostrictive soft material for mechanical energy harvesting and Carbon black dispersions as percolated flowable electrodes for capacitive energy storage are investigated.

In particular, the dielectric and electrical properties of these flowable dispersions are studied under static and dynamic conditions. The effect of the flow-rate on the local orientation and reorganization of the particles and their related dielectric and electrical behavior are examined.

Keywords : [Graphene oxide, Dielectric spectroscopy, Permittivity, Dielectric constant, Liquid crystals, Carbon black, Percolated Flowable Carbon Electrodes, Flow-Assisted Electrochemical Energy Storage, Electrochemical Flow Capacitors]