

**UNIVERSIDADE ESTADUAL DE CAMPINAS** FACULDADE DE ENGENHARIA ELÉTRICA E DE COMPUTAÇÃO

Rafael Felipe Vicentini

# Raman operando investigation on electrochemical double-layer capacitors

Estudo de Raman operando em capacitores eletroquímicos de dupla-camada

> Campinas 2023

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## Estudo de Raman operando em capacitores eletroquímicos de duplacamada

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Supervisor/Orientador: Prof. Dr. Hudson Giovani Zanin

Este exemplar corresponde à versão final da tese defendida pelo aluno Rafael Felipe Vicentini, e orientado pelo Prof. Dr. Hudson Giovani Zanin.

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Prof. Dr. Hudson Giovani Zanin (Presidente, FEEC/UNICAMP/BR)

Prof. Dr. Leonardo Morais da Silva (FACET/UFVJM/BR)

Dr. Bruno Guilherme Aguiar Freitas (FEEC/UNICAMP/BR)

Dr. Davi Marcelo Soares (Wichita State University/USA)

Dr. Lenon Henrique da Costa (IFSP/BR)

A ata de defesa, com as respectivas assinaturas dos membros da Comissão Julgadora, encontra-se no SIGA (Sistema de Fluxo de Dissertação/Tese) e na Secretaria de Pós-Graduação da Faculdade de Engenharia Elétrica e de Computação.

### Dedication

I express my gratitude to my parents, brother, and girlfriend for their unwavering support and motivation throughout my thesis journey.

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"(...) O caminho da cura pode ser a doença."

- (Racionais MC's)

### Abstract

Supercapacitors (SCs) play a crucial role in electrical energy storage applications, particularly when high power is required. To enhance and optimize these devices, extensive research has been conducted by the scientific community under operando conditions, employing various techniques such as Raman spectroscopy. This enables a unique glimpse into the inner workings of these devices during processes like charging and discharging. The first part of this study focuses on a comprehensive investigation employing computer simulations and Raman operando techniques using different aqueous electrolytes. By combining Raman operando and computer simulation, valuable insights are gained into the electrified electrode/electrolyte interface of SC devices. Subsequently, the second part presents a thorough electrochemical study aiming to understand the physicochemical properties of a SC utilizing a superconcentrated NaClO<sub>4</sub>-based electrolyte at different concentrations. This particular electrolyte, known as "water-in-salt electrolyte" or WiSE, significantly impacts the electrode/electrolyte interfaces. By substituting water dipoles with ions, the *working voltage* window (WVW) of SC devices can be effectively increased. Throughout the research, extensive characterization techniques such as Raman spectroscopy, scanning electron microscopy, and electrochemical studies were employed to analyze the materials involved. Moreover, our study stands out due to its simplicity, speed, high reproducibility, and low cost, making it a notable contribution in this field.

### Resumo

Os supercapacitores (SCs) desempenham um papel importante em aplicações de armazenamento de energia elétrica, especialmente quando é necessária alta potência. Para aprimorar e otimizar esses dispositivos, a comunidade científica tem realizado estudos em condições operando, utilizando diferentes técnicas, como a espectroscopia Raman. Essa abordagem permite investigar o funcionamento interno desses dispositivos durante processos como carga e descarga. A primeira parte deste estudo se concentra em uma investigação abrangente que combina simulações computacionais e técnicas de Raman operando, utilizando diferentes eletrólitos aquosos. Ao combinar Raman operando e simulação computacional, são obtidos informações valiosas sobre a interface eletrodo/eletrólito eletrificada dos dispositivos SC. Posteriormente, a segunda parte apresenta um estudo eletroquímico completo, visando entender as propriedades físico-químicas de um SC utilizando um eletrólito baseado em NaClO4 superconcentrado em diferentes concentrações. Esse eletrólito, conhecido como "eletrólito água-em-sal" ou WiSE, tem um impacto significativo nas interfaces eletrodo/eletrólito. Ao substituir os dipolos de água por íons, a faixa de tensão de operação dos dispositivos SC pode ser efetivamente aumentada. Ao longo da pesquisa, foram empregadas técnicas de caracterização, como espectroscopia Raman, microscopia eletrônica de varredura e estudos eletroquímicos, para analisar os materiais envolvidos. Além disso, nosso estudo se destaca pela sua simplicidade, rapidez, alta reprodutibilidade e baixo custo, sendo uma contribuição relevante nessa área.

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## Chapter 1 Introduction

*Supercapacitors* (SCs) are high-power energy storage devices that excel in delivering energy within seconds [1–4]. Their high capacitance and durability make them highly suitable for various commercial applications. In the electric vehicle sector, SCs are crucial for regenerative braking and high-power applications [2,5,6]. These unique characteristics are attributed to the composition of SCs, which rely on electrostatic processes and employ high-surface-area carbon electrodes immersed in ionic solutions, and in some cases, faradaic processes, which enhance electrochemical reactions. Therefore, studying and understanding the properties of these materials and electrolytes is essential for enhancing their electrochemical performance [7–12].

An area of intense focus and substantial contribution to this field revolves around the examination of supercapacitors under operando conditions, often referred to as "in-situ" studies. Regardless of the specific technique employed, whether it be Raman spectroscopy, X-ray diffraction (XRD), or transmission electron microscopy (TEM), these investigations illuminate the essential aspects of supercapacitors, emphasizing the pivotal role of these techniques in enhancing our comprehension of these energy storage devices [13–19]. For example, phase changes occurring at the electrode/electrolyte interfaces during electron transfer processes can be observed through shifts or the emergence of new bands in Raman or XRD spectra. These spectroscopic techniques provide valuable insights into the dynamic structural changes that take place during charge and discharge cycles, helping researchers to understand the underlying mechanisms better. When considering the three primary charge storage mechanisms, electrostatic double-layer (EDL) capacitance is primarily characterized by charge accumulation at the electrode-electrolyte interface without significant structural changes. In contrast, pseudocapacitance is linked to surface redox reactions, often associated with changes in oxidation states of transition metal ions within the electrode materials. These changes are readily detectable using techniques like XPS. Lastly, ion insertion, prevalent in many intercalation-based materials, leads to observable lattice expansion or contraction, which can be monitored using XRD and electron microscopy techniques [20]. Chapter 2 of this thesis addresses this topic by conducting a computational study using molecular dynamics simulations, which predicts changes in the electrified electrode/electrolyte interface. The results are then compared with Raman studies conducted under operando conditions using various aqueous electrolytes, including 1.0 M H<sub>2</sub>SO<sub>4</sub>, 1.0 M Li<sub>2</sub>SO<sub>4</sub>, 1.0 M Na<sub>2</sub>SO<sub>4</sub>, and 0.5 M K<sub>2</sub>SO<sub>4</sub>. Importantly, this study represents a collaborative effort involving computational simulation experts, and its primary contribution lies in the rigorous comparison between simulated data and "*in situ*" Raman analyses.

Additionally, extensive electrochemical studies are performed to gain deeper insights into the phenomena occurring at the electrified interface during ionic adsorption and desorption processes. These studies demonstrate that electrochemical processes are not solely governed by electrostatic interactions but are primarily influenced by sulfate insertion ( $SO_4^{2-}$ ). Moreover, the electrostatic process manifests as a shift in the D-band observed in Raman operando spectra, indicating the surface accumulation of ionic species present in the aqueous electrolyte [21].

Although these aqueous-based devices exhibit high capacitance and durability, their energy density remains low due to the thermodynamic barrier associated with water molecule dissociation beyond a *working voltage window* (WVW) of 1.23 V *vs. Standard Hydrogen Electrode* (SHE). This voltage threshold marks the point at which the energy required for water splitting exceeds the energy storage capacity of the device, resulting in the undesired evolution of oxygen and hydrogen gases. Overcoming this limitation is a critical challenge in the development of aqueous energy storage systems with higher energy densities [22]. Consequently, the scientific community has been actively exploring alternatives to traditional aqueous systems. One promising alternative is the use of "*water-in-salt electrolytes*" or WiSE, which involves adding significant amounts of salt to the solution while adhering to its solubility limit [21,23–36]. This substitution of water dipoles with ions forms a protective layer at the electrode/electrolyte interface, enabling operation at higher voltages.

In this context, **Chapter 3** presents a Raman study conducted under operating conditions using NaClO<sub>4</sub> electrolyte at different concentrations: 1 m, 5 m, 10 m and 17 m. The study incorporates both constant voltage conditions (chronopotentiometry studies) and dynamic voltage conditions (cyclic voltammetry studies). Through precise electrochemical investigations and Raman operando analysis, the real voltage limits and the effectiveness of WiSE in enhancing the commercial viability of aqueous electrolytes are examined. Furthermore, **Chapter 3** explores the influence of WiSE concentration on the WVW of SCs and reveals how electrolyte properties impact the *electrical double layer* (EDL) and its physicochemical properties [37].

Lastly, it is worth mentioning that **Chapters 2** and **3** present the complete versions of papers previously published in reputable journals. **Chapter 2**, published in the Elsevier Journal of Energy Chemistry with an Impact Factor of 13.1 (CiteScore: 19.1), offers significant insights into the field. Likewise, **Chapter 3**, published in the Journal of Applied Materials and Interfaces with an Impact Factor of 9.5 (CiteScore: 15.7), contributes valuable findings [21,37]. I am grateful for the permission granted by the copyright holders to include these publications in my thesis. For additional information, please refer to the appendix section.

## Chapter 2

Raman probing carbon & aqueous electrolytes interfaces and molecular dynamics simulations towards understanding electrochemical properties under polarization conditions in supercapacitors

## 2.1. Introduction

Electrochemical supercapacitors (ESs) are energy storage devices based on the use of porous electrode materials immersed in an electrolyte to provide a rapid charge-storage process at the solid/liquid interface [1–4]. As a result, ESs are vital for several different technological applications where a very high specific power (P/W kg<sup>-1</sup>) is demanded, as is the case of the modern electric cars [2,5,6]. In this sense, the operation principle of these devices is based on the intimate separation of the electronic and ionic surface charges in the complex molecular structure known as the electrical double-layer (EDL) [38,39]. Several important fundamental and technological aspects of ESs were extensively discussed in diverse important books published in the last three decades [7–12].

In general, ESs can store energy in both the interfacial electric field (*e.g.*, charge accommodation process) and Faradaic (*e.g.*, pseudocapacitive processes involving the electron transfer) processes. Electrical double-layer capacitors (EDLCs) are known to store charge very quickly by ions adsorption at the electrode/electrolyte interface covered by a carpet of water dipoles resulting in an ionic surface excess ( $\wp_{ions}$ ). The EDL structure has its 'first layer' (*e.g.*,

inner Helmholtz plane, IHP) in aqueous solutions composed of strongly oriented (saturated) water dipoles separating the electronic and ionic phases. Eventually, some ions can invade the dipole layer resulting in the *specific adsorption phenomena* (*e.g.*, direct contact between the non-solvated ion and the electronic conductor). The 'second layer' (*e.g.*, outer Helmholtz plane, OHP) comprises the surface arrangement of the hydrated ionic species strongly attached to the first (dipole) layer. The 'third layer' (*e.g.*, Gouy-Chapman layer, GC) connecting the 'rigid' part of the interface with the solution bulk is characterized by its diffusive character imposed by the thermal energy. The average thickness of this layer depends on the electrolyte concentrations.[40] At high concentrations (*e.g.*, > 0.1 M), the thickness of the G-C layer is sharply decreased and, therefore, the overall interfacial capacitance measured in practice is dictated only by the compact Helmholtz layer, *i.e.*, the lowest capacitance 'connected' in series. An exception is the semiconductor materials where a small 'space-charge' or 'quantum' capacitance confined inside of the electrode structure dominates over the distinct electrode capacitances connected in series [41].

For several different conducting electrode materials, the dipoles arrangement in the IHP and the solvated ionic species present in the OHP govern the overall dielectric properties of the electrified interface, thus directly affecting the capacitance exhibited by electrical double-layer capacitors (EDLCs).[42] On the contrary, pseudocapacitors, like some battery-like systems, exhibit a pronounced charge-transfer at the electrode/electrolyte interface (*e.g.*, faradaic reactions such as intercalation, and reversible solid-state redox reactions) [43].

From these considerations, several attempts have been made for studying the EDL properties, mostly using the electrochemical techniques [38]. Only recently other spectroscopy techniques (*e.g.*, Raman, XRD) have been used *in-situ* for studying the electronic, structural, and chemical properties of the electrode/electrolyte interface under polarization conditions.<sup>[19–24]</sup> In this sense, the *in-situ* or *operando* Raman technique has helped to elucidate different important phenomena occurring during the dynamic charge-storage processes involving different carbon-based electrode materials. In principle, this technique can be used to track effects on the electrode material during the intercalation reactions and redox processes. For example, in lithium-ion energy storage devices, graphite works as the negative host material with the formation of  $\text{LiC}_6$  due to lithium intercalation. During this process, the G-band position could shift its position from 1580 cm<sup>-1</sup> to 1590 cm<sup>-1</sup> due to change in force constants of the inplane C–C bonds. Besides, the G-band can also become broaden and split as a consequence of new crystallography arrangements, *i.e.*, when the intercalation of Li<sup>+</sup> into graphite interplanar

space promotes the formation of a new phase containing the Li-C composite. The D-peak presents a different path, weakened, and broadened due to the solid electrolyte interface (SEI). Analyzing the effect of ions size, Hardwick *et al.* assembled supercapacitor systems using large ions to compose the electrolyte. These author showed that the graphite G-band has a doublet  $(e.g., E_{2g2}(i) (1578 \text{ cm}^{-1}) \text{ and } E_{2g2}(b) (1600 \text{ cm}^{-1}))$  when large ions such as  $Et_4N^+$  and  $BF_4^-$  are (de)intercalated into the graphite interplanar crystalline structure. This fact also caused a lattice damage with increasing of the graphite D-peak.

Graphite has been extensively studied, and its Raman spectra have been explained and modeled in the last four decades [13–15,44]. Thus, according to the literature, there is some consensus about structural disorder and its impact on the graphene properties. Graphene can be represented as a single-layer of graphite that exhibits a two-dimensional structure. For the sake of modeling, we present in Figure 1(a) the Brillouin zones of graphene as hexagons, and a scheme of Dirac cones at the K points (corners of the hexagon) describing the electronic dispersion.



**Figure 1.** Schematic representation of the (a) Brillouin zone; (b) D-peak; and (c) 2D double-resonance process of graphene.

Optical phonons at K and  $\Gamma$  points are the phonons responsible for the Raman D and Gpeaks, respectively, in sp<sup>2</sup> carbons. G-peak is an  $E_{2g}$  optical mode centered at 1582 cm<sup>-1</sup>, originated by doubly degenerate vibrational mode of iLO (in-plane longitudinal optical) and iTO (in-plane transversal optical) phonon branches crossing at the  $\Gamma$  point in the graphite first Brillouin zone [45,46]. The G-peak corresponds to the high-frequency  $E_{2g}$  phonon at  $\Gamma$ . D-peak is originated from the breathing modes of six-atom rings, associated with the LO (longitudinal optical) phonon at the K point of the Brillouin zone. Since this peak originated from a phonon mode at the edge of the Brillouin zone, a defect is required in the scattering process for the momentum conservation. Thus, the D-peak on Raman spectra of graphite is activated by the structural disorder, which is generally concentrated at its edges [44-47]. D-peak appears when lattice vibration (e.g., Raman-inactive process) hit a defect causing the breaking of symmetry and affecting the selection rules (q = 0) required for first-order Raman peaks. D-peak originated from an inter-valley double resonance Raman scattering involving the LO phonon at K point and a defect, as shown by **Figure 1**(b). Its frequency is dispersive with excitation wavelength, varying about 50  $\text{cm}^{-1}$  eV<sup>-1</sup>, due to the double resonance mechanism and the dispersion of the LO phonon near the K point. Moreover, the frequency of the LO phonon branch at the K point is lowered by the Kohn anomaly. The strong electron-phonon coupling near the Fermi level (K points) causes a change in the screening of lattice vibrations softening the phonon frequency. In the case of 2D-peak, it is a D-peak overtone. Here, defects are unnecessary, since momentum conservation is satisfied by two phonons with opposite wave vectors (Figure 1(c)).

Different electrochemical applications involving energy storage processes extensively employ carbon-based materials due to its excellent chemical stability and good conductivity. Under dynamic polarization conditions with proper cells, it is possible to disperse the D-peak and 2D-peak imposing a proper shift along with the Fermi level by surface transfer doping (STD), which may occur due to adsorption of the ionic species in the electrical double-layer structure or charge-transfer reactions between electrode and surface adsorbates [48]. The adsorption energy of an adsorbed ion could be as high as the material work function, trapping charges (*i.e.*, adsorption energy of Na<sup>+</sup> adsorbed onto graphene nanosheets may be as high as 3.6 eV and work function of ~ 4 to 4.5 eV) and could reduce mobility inside the crystal. The charge transfer depends on the electrochemical potential at an interface and relative positions of the electrode Fermi level and redox potential of the species in solution [49]. At the electrode/electrolyte interface, if the reduction potential of the electrolyte species present in the compact Helmholtz layer lies lower than the Fermi level energy of the electrode, electrons will flow from the electrode to the adsorbates (*e.g.*, ions or molecules) and in the opposite direction if the oxidation potential of the electrolyte species at positive potentials lies above [50].

Although a joint operando Raman-electrochemistry investigation comprises a powerful tool to investigate structural and electronic properties of carbon-based electrodes, materials modeling can predict complex behavior and predict material properties from a molecular framework [13–15]. In this sense, computational materials science has a spotlight elucidating complex interface phenomena, such as electrochemical double-layer [44]. Among several levels of computations, molecular dynamics (MD) have been obtaining the best agreement between experimental and theoretical data. Jiang et al. studied the EDL capacitance of graphene electrodes in mono-valent (e.g., Na<sup>+</sup> and K<sup>+</sup>) aqueous electrolytes using MD simulations. According to these authors [13–15], the change of water dielectric constant in different electrolytes largely cancels the variance in electric potential drop across the EDL in the presence of different cations. The authors also obtained agreement between experimental and theoretical capacitance values. Nevertheless, not only electrochemical data can be used to joint MDmodels. Given the recent development of high spatial resolution in-situ electrochemical fluid cells for scanning transmission electron microscopy (STEM), the formation and dynamics of the EDL using *in-situ* STEM and MD can be observed. In this sense, Reich and Thomsen [46] observed that Gouy-Chapman and modified Helmholtz models can predict poorer image quality than MD simulations. However, in most of the literature reported, the dynamics of EDLCs are assessed using the *in-situ* (operando) Raman and MD simulations.

In this study, for the first time, the unusual and intriguing phenomenon related to the shift of the D-peak was explored in operando Raman analysis. This phenomenon occurs during the surface accumulation of ionic species in an aqueous electrolyte. Additionally, we explore its modeling through molecular dynamic simulations. Moreover, our finds show the overall capacitance of sulfate-based aqueous SCs is not only governed for electrostatic interaction, but it mainly occurs owing to the sulfate insertion process. In summary, this work presents new insights into the charge-storage mechanism of aqueous-based capacitors.

## 2.2. Experimental and theoretical methods

### 2.2.1. Experimental methods

Electrodes were prepared by cutting a graphite bar (MG2 graphite from CM Carbon Co. (China)) into discs of 1.6 and 0.8 cm of diameter. The graphite discs were polished using the #400 to 1200 grit emery papers and finalized with Al<sub>2</sub>O<sub>3</sub> in a metallographic polishing cloth. After that, the graphite discs were copiously washed with deionized water. The polished graphite surface had a small hole with 0.2 cm of diameter to enable Raman laser to go through and reach the electrochemically active surface regions of the graphite *working electrode* (WE) polarized in relation to the graphite *counter electrode* (CE). These electrodes were geometrically disposed of face-to-face and close enough to propitiate an almost uniform distribution of the electric field. To avoid short circuit, a mesoporous membrane soaked with the electrolyte containing a small hole was used as the separator. In this setup, the CE and the reference electrode cable from the potentiostat were short-circuited (equipotential conditions).

Electrolytes were obtained from the 1.0 M H<sub>2</sub>SO<sub>4</sub>, 1.0 M Li<sub>2</sub>SO<sub>4</sub>, 1.0 M Na<sub>2</sub>SO<sub>4</sub>, and 0.5 M K<sub>2</sub>SO<sub>4</sub> aqueous solutions used to fill the space between the WE and CE housed in the specially designed electrochemical cell containing a glass window (Please see schematic in **Figure S1**). Its moderate solubility limited the particular concentration of 0.5 M used for K<sub>2</sub>SO<sub>4</sub>. **Figure S1**(a) shows the cell coupled with the Raman microscope, while Figure S1(b) presents details of the internal cell components. After providing vacuum conditions, a 20- $\mu$ L syringe was used to introduce the electrolyte into the cell which was immediately sealed to avoid contact with the atmosphere.

To check if the assembled electrochemical cell containing the graphite electrodes behaves like an electrochemical capacitor, we first investigated the cell's electrochemical response. Before starting the electrochemical tests, a thousand cyclic voltammograms at 1000 mV s<sup>-1</sup> was carried out to promote the appropriate wettability conditions, and the stability of the electrode response. It was performed different cyclic voltammograms at different scan rates of 20, 50, and 100 mV s<sup>-1</sup>. Different working voltage windows were verified for the different electrolytes. We accomplished *electrochemical impedance spectroscopy* (EIS) experiments (*e.g.*, 10 kHz to 10 mHz and  $\Delta E = 10$  mV (peak-to-peak)) in the middle of the capacitive voltage window previously verified in the *cyclic voltammetry* (CV) experiments. Furthermore, *galvanostatic charge-discharge* (GCD) experiments applying the values of the average voltammetric currents verified at 100 mV s<sup>-1</sup> (*e.g.*,  $\approx$  0.2 to 0.3 mA cm<sup>-2</sup>) were conducted to provide additional/complementary electrochemical findings. A VersaSTAT 4 potentiostat-galvanostat from Ametek was used throughout.

The Raman spectra acquisition in the *operando* studies were obtained while the CV experiment was running at a scan rate of  $1.0 \text{ mV s}^{-1}$ . The Raman spectroscopic acquisition time for each spectrum was 60 s with 2 accumulations. For each voltage increment of 0.2 V, the Raman spectrum was acquired to cover each particular electrolyte's entire working voltage window. Spectra were obtained using a Renishaw Raman Spectrometer equipped with 785 nm (1.58 eV), 633 nm (1.96 eV), 514.5 nm (2.41 eV) and 488 nm (2.54 eV) wavelength lasers.

### 2.2.2. Molecular Dynamics simulations

The simulated electrochemical systems were based on a theoretical model considering different monovalent ionic species in contact with mesoscopic slit pores formed between the graphite layers. **Figure 2** illustrates the system in a simplified sketch.



Figure 2. Schematic representation of the system simulated.

Four layers of graphite were used to represent each electrode (*e.g.*, anode and cathode), forming a symmetric box filled with the different electrolytes. Each layer was composed by 336 carbon atoms. Three aqueous electrolytes were evaluated: Li<sub>2</sub>SO<sub>4</sub> 1.0 <sub>M</sub>, Na<sub>2</sub>SO<sub>4</sub> 1.0 <sub>M</sub>, and K<sub>2</sub>SO<sub>4</sub> 0.5 M. The following number of molecules was considered: [2220/80/40] for water, Li<sup>+</sup> or Na<sup>+</sup>, and SO<sub>4</sub><sup>2-</sup>, and [2220/40/20] for water, K<sup>+</sup> and SO<sub>4</sub><sup>2-</sup>, respectively. The molecules were assembled with Packmol [43]. Molecular dynamics (MD) simulations were performed using LAMMPS software.[51] Force field parameters for cations were taken from Madrid-2019 force field [52], and for the anion, GAFF (General Amber Force Field) was used for bonded forces [53] and Madrid-2019 force field [52] parameters for non-bonded interactions. Charge distributions regarding the cations and anions were taken from Madrid-2019 force field [52].

The graphite Lennard-Jones (LJ) parameters were taken from Beu et al. [54]. The TIP4P/2005 model [55] was used for water, which was kept rigid with SHAKE algorithm implemented in LAMMPS [56]. The LJ parameters for unlike atoms were obtained by Lorentz-Berthelot combining rules. More details concerning the force fields parameters used in this work are presented in Tables S1 and S2 of the Supplementary Information. The parallel plates had dimensions of 29.49/31.19 Å in X/Y directions. The distance between the electrodes was set to 80 Å to keep bulk-like behavior at the center of the system, *i.e.*, this distance is practically four times the length of the electrical double-layer (EDL) encountered for concentrated electrolytes  $(e.g., \approx 20$  Å). In this sense, considering the two EDL of the symmetrically disposed of electrodes facing each other, the bulk region has a length of  $\approx 40$  Å. Periodic boundary conditions were applied to all directions, and unwanted interactions were treated using subroutines implemented in LAMMPS [57,58]. Carbon atoms were fixed, and a single charge was added to each atom of the inner layer wall, which was balanced by the addition of the opposite charge to the parallel wall. The charges were selected to result in electric charge densities of -2.245, -4.850, and -9.700 µC cm-2 at the negative electrode. All MD simulations were run in NVT ensemble at 298.15 K and 1.0 atm. The simulations were carried out for 70 ns, being the first 50 ns discarded as equilibration time. Block-averaging was applied to the production run to calculate the standard deviations; each block was 4 ns longer, data were stored at every 5 fs and the simulation time step was set to 1 fs.

It is important to mention that the first part of this study consisted on the force field set evaluation. To verify the efficiency of the force field to capture experimental behavior of the water solutions used in this work, bulk simulation of the electrolytes with the same size described above were carried out. The methodology used to run MD simulations, as well as to calculate the transport properties, can be found elsewhere [59]. Figure 3 presents the results, good agreement is observed for all properties in comparison with experimental data. The comparison of our findings with simulated results from Zeron *et al.* [52] show a better performance of our force field combination. This analysis corroborates the ability of our force field combination to predict experimental nature with good accuracy.



**Figure 3.** Force field validation for  $1 \text{ M Li}_2\text{SO}_4$ ,  $1 \text{ M Na}_2\text{SO}_4$  and  $0.5 \text{ M K}_2\text{SO}_4$  electrolyte compositions: (a) and (b) self-diffusion coefficient for cation and anion, respectively, (c) viscosity and (d) density. Experimental measures were taken from[60–64] and references therein. Simulated results were taken from Zeron *et al.*[52] System size correction from Yeh and Hummer[65] was applied to diffusivity.

## 2.3. Results and discussion

# **2.3.1.** Analysis of the electrochemical findings obtained for the graphite electrode in different electrolytes

Early studies using graphite electrodes (*e.g.*, the bulk analogy of graphene) provided a platform for investigating the charge-storage process in different carbon-based electrode materials [66]. The fundamental works involving the *stress-annealed pyrolytic graphite* (SAPG) electrodes were accomplished by Bauer *et al.* [67], Randin and Yeager [68], and Gerischer [69,70]. A significant breakthrough was presented by Gerischer, who presented a comprehensive theoretical study to explain the interface capacitance exhibited by the SAPG electrodes in terms of the electronic density of states (DOS) located around the Fermi level. Despite these considerations, detailed experimental studies involving the conventional graphite electrodes (CGE) is rather scarce.

An important issue regarding the different graphite electrodes is concerned with the electrochemical response reproducibility. In short, several essential works reported the necessity to use good quality and well-characterized graphite materials to obtain meaningful electrochemical findings [71–73]. For instance, the cleavage method and quality of the graphite electrode can result in surfaces with different step densities and hence the number of exposed edges, which, in turn, can affect the electrochemical response. CGE can be quite porous since the graphite layers are inhomogeneously distributed.

Before the *in-situ* Raman studies (*operando* analysis) under polarization conditions, techniques to evaluate the reproducibility of the electrochemical findings in the different electrolytes were accomplished in the current work with the CGE different preliminary electrochemical studies using the *cyclic voltammetry* (CV), *electrochemical impedance spectroscopy* (EIS), and *galvanostatic charge-discharge* (GCD). To equalize the initial surface conditions, the electrochemical cell was first preconditioned by applying a thousand charge-discharge cycles at 1000 mV s<sup>-1</sup> using the CV technique.



Figure 4. Electrochemical findings obtained for CGE in different electrolytes.

The different electrochemical data are gathered in **Figure 4**. For the different electrolytes, excellent capacitive properties for the CGE were verified. The CV profiles are almost rectangular and quite similar, while the working voltage window slightly depends on the particular electrolyte. In principle, these findings indicate similar charge-storage capabilities for the different monovalent cationic species (Please see further discussion). The analysis of

the EIS findings revealed typical capacitive electrode behavior exhibiting the frequency dispersion phenomenon due to the surface heterogeneities at the atomic level [38]. Accordingly, the GCD plots exhibited the triangular shape expected for well-behaved capacitor materials. The experimental values of the 'apparent' areal *electrical double-layer* (EDL) capacitance  $(C_{edl})$  accounting for the CGE/solution interface as a function of the electrolyte composition are gathered in **Table 1**.

Electrolyte	Cedl (CV)	$C_{\mathrm{edl}}\left(\mathrm{EIS} ight)$	Cedl (GCD)
	$[\mathrm{mF}\mathrm{cm}^{-2}]$	$[\mathrm{mF}\mathrm{cm}^{-2}]$	$[\mathrm{mF}\mathrm{cm}^{-2}]$
1.0 M H <sub>2</sub> SO <sub>4</sub>	2.31	2.13	2.10
1.0 M Na <sub>2</sub> SO <sub>4</sub>	2.00	1.95	1.96
1.0 M Li <sub>2</sub> SO <sub>4</sub>	1.63	1.54	1.57
0.5 M K <sub>2</sub> SO <sub>4</sub>	1.67	1.58	1.57

**Table 1.** Electrical double-layer capacitance as a function of the electrolyte composition.

The capacitance values were slightly affected by the presence of different monovalent cationic species, exhibiting values in the range of 1.54 to 2.31 mF cm<sup>-2</sup>. A particularly good correspondence was observed for the capacitances determined using the different electrochemical techniques (e.g., CV, EIS, and GCD). While the SAPG electrodes commonly exhibit a very small areal capacitance of ~ 3 to 7  $\mu$ F cm<sup>-2</sup> [69,70], which is a characteristic of the space-charge (quantum) structure formed inside the semimetallic carbon material, in the present study, using CGE, the capacitance values were practically a thousand times higher, *i.e.*, the *electrical double-layer capacitance* referring to the compact Helmholtz layer formed on the solution side dominates the overall capacitance. Figure S2 shows the SEM image of the polished graphite surface used in the present study, which is highly rough and, therefore, the areal capacitance values were determined considering as the normalizing factor the geometric surface area multiplied by the roughness factor determined using cyclic voltammetry, *i.e.*, the study based on the Randles-Sevcik equation using a 5.0 mM  $Ru(NH_3)e^{-2/-3}$  solution as the redox probe dissolved in the 0.5 M Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte revealed a roughness factor of 1.57 for the graphite electrode during the reversible outer-sphere redox reaction. Therefore, the high capacitance values reported above in the absence of a redox reaction cannot be entirely attributed to the rough/porous nature of the electrode material (Please see further discussion).

In this sense, some type of insertion/extraction mechanism involving the ionic species from the electrolyte must be present to strongly enhance the overall capacitance (Please see further discussion). In the case of SAPG (or HOPG) electrodes, this type of mechanism contributing to the capacitance is absent due to the compact nature of the pyrolytic carbon material.

The resistivity of CGE is  $1.05 \times 10^{-3} \Omega$  m according to the impedance method used in the present study where the *d.c.* limit of the real impedance was measured at 10 mHz and good convergence of the resistance values was observed for frequencies lower than 10 Hz. On the contrary, in the case of SAPG, we must consider the existence of a considerable anisotropic behavior (*e.g.*, ~1.1 × 10<sup>-3</sup>  $\Omega$  m (*c*-axis) and ~ 5.0 × 10<sup>-7</sup>  $\Omega$  m (*a*-axis)) [74,75]. To quote, the resistivity of different metals is in the range of (1.6-98)  $\cdot$  10<sup>-8</sup>  $\Omega$  m. Therefore, the anisotropic behavior is commonly linked to the space charge behavior exhibited by the SAPG while the effective resistance of the material has different paths in the case of polycrystalline SAPGs [69,70,74,75].

### 2.3.2. Analysis of the in-situ (operando) Raman studies

**Figure 5**(a) presents Raman spectra of graphite under dynamic conditions (*operando*) in the electrochemical capacitor filled with 1.0 H<sub>2</sub>SO<sub>4</sub>, obtained with 785 nm excitation laser wavelength. The spectra are characterized by the presence of the first-order G-peak and the defect-induced D- and D'-peaks, originated by intervalley and intravalley double-resonance processes, respectively, involving a phonon and a defect. Figure 3(b) shows the analysis of the spectrum with the G, D, and D' peaks fitted by Lorentzian curves. It is observed in **Figure 5**(a) a shift in the D-peak position when the external electric potential is applied to the capacitor. A reversible blue shift is observed during the charge-discharge process. For a detailed view of this phenomenon, **Figure 5**(c) presents the D-peak position obtained from the peak fitting as a function of the applied potential. The D-peak shifts its position from 1308.3 to 1312.5 cm<sup>-1</sup> during charge, and from 1312.5 to 1308.5 cm<sup>-1</sup> during discharge, which gives us ~4 cm<sup>-1</sup> V<sup>-1</sup>. On the other hand, G- and D'-peaks have negligible shifts as can be seen in **Figure 5**(a).

**Figure 5**(d) presents the behavior of the 2D band, at ~2615 cm<sup>-1</sup>, with the changing in the applied ptental to the capacitor. The 2D-peak is the D-peak overtone and it is originated from an intervalley double-resonance process involving two-phonon (**Figure 1**(c)). Although the D-peak is defect-induced, defects are unnecessary for the observation of the 2D-peak. Similarly, to what happens to the D-peak, a reversible blue-shift happens for the 2D-peak when an external potential is applied to the electrochemical cell. To check the magnitude of this shift,

we performed a fitting of the 2D-peak using two Lorentzian curves, which was indicated in **Figure 5**(e) as the 2D<sub>1</sub> and 2D<sub>2</sub> peaks. The 2D<sub>1</sub> and 2D<sub>2</sub>-peaks position were then plotted in **Figure 5**(f) as a function of the applied potential. The reversible blue-shift of both 2D-peak components is clearly observed during the charge-discharge process. In this case, the shifts observed for the 2D<sub>1</sub> and 2D<sub>2</sub>-peaks are ~9 and 10 cm<sup>-1</sup> V<sup>-1</sup>, respectively, around twice the ones observed for the D-peak, such as expected since this peak is a D-peak overtone.



**Figure 5.** First-order (a & b) and second-order (d & e) Raman spectra of graphite under dynamic polarization conditions (c & f). Changes in the peak position and intensity are plotted against the scanned cell voltage. Spectra were taken by applying 785 nm excitation laser wavelength during cyclic voltammetry experiments performed at 1.0 mV s<sup>-1</sup> in 1.0 M H<sub>2</sub>SO<sub>4</sub>. On the average, Raman spectra were taken for each 0.2 V voltage increment.

The reversible shifts verified for the D- and 2D-peaks with the applied potential can also be explained considering a Kohn anomaly reduction when the electrode is charged. The strong electron-phonon coupling on the  $A_{1g}$  phonons at the K point cause a softening in the phonon frequency evidenced by a kink in LO phonon branch at the K point. This phenomenon is known as Kohn anomaly [14]. When a potential is applied to the graphite electrodes, there is a change in the Fermi level, which in turn reduces the electron-phonon interactions, and the screening in the lattice vibrations caused by the Kohn anomaly. Since the screening effect is reduced, the softening of the phonon is reduced and its frequency is increased. In this case, the shift in the 2D-peak is expected to be twice that verified for the D-peak because the 2D-peak corresponds to a sum of two D-peak phonons. The electron-phonon coupling on the E<sub>2g</sub> phonon at the  $\Gamma$  point is much weaker than the one on the  $A_{1g}$  phonon at the K point [76]. This may be the reason why the same shift on the Raman frequency is not observed for the G band.

As shown in **Figure 5**(a) and (d), blue shifts of both D and 2D bands are observed by applying a voltage difference between the WE and CE, that forces the solvated ions to accumulate at the interface. On the contrary, as seen in **Figure 6**, the applied voltage in the absence of an electrolyte is not causing the shift in the D-peak position. Thus, there is strong evidence that the presence of the ionic species is the leading cause of the observed effects in the Raman spectra, *i.e.*, the ions in the presence of an electric field might reversibly insertion between the graphene layers of graphite, resulting in structural defects or lattice stress. As reported by Inaba *et al.* [77], the spectral changes verified in the Raman studies are associated with the phase transitions that occur reversibly during the charge-discharge cycles. On the whole, these authors reported that the electrochemical intercalation process is determined by the surface stage of graphite intercalation compounds, *i.e.*, on the stage dependence of the relative intensities of the Raman signals referring to the 'interior' (E<sub>2g2</sub><sup>(i)</sup>) and 'bounding' (E<sub>2g2</sub><sup>(b)</sup>) layer modes.

From another perspective, the cations adsorption might result in the trapping of electrons present in the conduction band with the creation of a "hole" in the solid structure (*e.g.*, the freeelectron absence). Even more pronounced than electrostatic adsorption, ions with electronwithdrawing or donating potential such as  $M^+$  (*e.g.*,  $H^+$ ,  $Li^+$ ,  $Na^+$ , and  $K^+$ ) can also trap charges altering their concentrations in the EDL and consequently changing the local electric field.



**Figure 6.** Effect of the (a & b) cell voltage on the Raman first-order spectra during dynamic conditions in the absence of an electrolyte inside the cell (*e.g.*, there is no variation on the D-peak position).

Different electrolytes and different excitation wavelengths were explored (*e.g.*, 785, 633, 514, and 488 nm) to achieve a better understanding of the Raman behavior accounting for the ionic effect on the charge-storage process. All Raman spectra are presented in **Figure S3**. The findings in **Figure S3**(a) repeats those of **Figure 3**(a) for the sake of a more straightforward comparison. **Figure 7** shows the Raman frequency shifts ( $\Delta \omega = \omega_V - \omega_0$ ), the difference between the frequency at a given applied voltage ( $\omega_V$ ) and the frequency at 0V ( $\omega_0$ ), observed for the graphite D-peak as a function of the applied voltage and the electrolyte composition.



**Figure 7.** Raman frequency shifts  $(\Delta \omega)$  observed for the D-peak (a-d) as a function of the applied voltage and the electrolyte composition, using different excitation wavelengths. Data were extracted from the spectra in **Figure S3**.

The different electrolytes and laser conditions are indicated in the plots of **Figure 7**. It is possible to observe in **Figure 7**(a) for the studied cations (*e.g.*,  $Li^+$ ,  $Na^+$ , and  $K^+$ ) that  $Li^+$  incurred in a higher Raman shift as a function of cell voltage. In principle, these findings

indicate more pronounced intercalation of the smaller  $Li^+$  ions with corresponding change/distortion in the graphite structure even considering that the experimental electrical double-layer capacitance was practically the same for the different electrolytes (see **Table 1**). The Stokes radii incorporating the hydration/solvation shell are  $Li^+$  (239 pm) > Na<sup>+</sup> (183 pm) > K<sup>+</sup> (125 pm) while the crystal ionic radii for the bare ions are  $Li^+$  (90 pm) < Na<sup>+</sup> (116 pm) < K<sup>+</sup> (152 pm) [78]. Therefore, one can propose that the Li<sup>+</sup>-ions partially lose their hydration shell resulting in a facilitated insertion process between the graphene layers accessible by the electrolyte or the solvated Li<sup>+</sup>-ions resulted in a more drastic lattice displacement leading to structural defects during the applied voltage. Consequently, a higher wavenumber shift during the *operando* Raman can be observed.

Some 'asymmetric effects' related to the  $\Delta \omega$  vs. voltage profiles were obtained during the charge-discharge of the different ionic species. In principle, one can understand the appearance of these asymmetries considering the different structural defects occurring in the first graphene layers of graphite due to the intercalation of the different hydrated and nonhydrated (bare) ions. First, one has for the hydrated anions and cations that the latter exhibit different 'volumetric charge densities', which are enclosed by the first hydration shells containing the strongly oriented water dipoles [79]. Therefore, the positive and negative ions with different effective sizes can result in different intercalation processes with corresponding changes in the structural defects. More than 90% of the electrode surface is covered by the strongly oriented (saturated) water dipoles since the solvent is present at a very high concentration of ~56 M [79]. However, since in general, the energy involved in the anions solvation is not as high as to cationic species, some anions can undergo a 'specific adsorption process' where the oriented dipole layer is partially replaced by the bare anions that lose their hydration shell [80]. This specific process is a very short-range chemical interaction that prevails over the short-range electrostatic forces [80]. As a result, these smaller (bare) anions can also contribute to further structural defects incurred through a specific intercalation process. Thus, these combined intercalation effects involving hydrated and non-hydrated ionic species can result in asymmetries for the charge-discharge processes.

# **2.3.3.** Theoretical analysis of the electrified graphite/solution interface using molecular dynamics (MD) simulations

# **2.3.3.1.** Fundamental properties of the electrified carbon/electrolyte interface

The electrical double-layers (EDLs) formed at the carbon/solution interface have been studied by different authors using different theoretical approaches (*e.g.*, continuum modeling, Molecular Dynamics, Grand-Canonical Monte Carlo, and Density Functional Theory).[81–90] In several cases, the theoretical analyses are accomplished using the Stern's theory where the compact Helmholtz (H) layer subjected to a strong electric field (*e.g.*, ~ 10<sup>7</sup> V cm<sup>-1</sup>) is in series with the diffuse Gouy-Chapman (GC) layer where both the electric and thermal effects are present. Also, the capacitance exhibited by the GC-layer (*C*<sub>GC</sub>) depends on the inverse of the absolute temperature and the square root of the electrolyte concentration (*e.g.*, *C*<sub>GC</sub>  $\alpha$ [ions]<sup>1/2</sup>/*T*), while the compact H-layer is unaffected by these variables [79]. For concentrated electrolytes (*e.g.*, [ions] > 0.1 M), the lower capacitance exhibited by the Helmholtz layer dictates the overall capacitive effects measured in practice (*e.g.*, *C*<sub>overall</sub><sup>-1</sup> = *C*<sub>H</sub><sup>-1</sup> + *C*<sub>GC</sub><sup>-1</sup>, and *C*<sub>overall</sub>  $\cong$  *C*<sub>H</sub>) [80].

Some authors have verified that the ion nature exerts an essential role in determining the ionic distribution in the electrolyte side of the interface region [89]. Besides, the complex changes in the local dielectric constant ( $\varepsilon$  (x)) for the different layers (*e.g.*,  $C_{\rm H} \propto \varepsilon$  (x) and  $C_{\rm GC} \propto (\varepsilon(x))^{1/2}$ ) caused by the differently oriented water dipoles allied to the presence of the specific ionic adsorption phenomenon add a high degree of complexity for the theoretical analysis involving the EDLs in aqueous medium [80]. Hence, even using modern computers, several simplifications regarding the EDL models are commonly adopted in practice [42]. Thus, essential aspects as the local changes of the dielectric constant, the presence of specifically adsorbed anions, the presence of redox-active functional surface groups in carbon materials, and the non-uniform surface electric field caused by the inhomogeneous surface morphology are challenging difficult to consider in a single (unique) EDL theoretical model [91–93].

Considering an assembly of small slabs (*e.g.*, 0.005 nm) along the direction (*x*) perpendicular to the electrode surface, the local electric potential V(x) is described by the following fundamental differential equation: [89]

$$\frac{\partial^2 V(x)}{\partial x^2} = -\frac{q(x)}{2A_G \varepsilon_0},$$
(2)

where q(x) is the overall local charge stored at the distance *x*, *A*<sub>G</sub> is the area of the slab used in the MD simulation, and  $\varepsilon_0$  is the vacuum dielectric constant.

From the symmetry condition where V(x) in the center of the rectangular box (*e.g.*,  $x = \pm L/2$ ) is considered as a reference (*e.g.*, dV/dx = 0 at  $x = \pm L/2$ ), the following relationship gives the V(x)-dependency:

$$V(x) = -\iint_{L/2}^{x} \frac{q(x)}{2A_{G}\varepsilon_{0}} dx^{2},$$
(3)

where the numerical integration yields the desired V(x) and q(x) dependencies. Equation (3) can be solved numerically using different standard methods (*e.g.*, one-side Green's function, finite differences, and discrete Fourier transform). A comparison of these different methods was reported by Wang *et al.* [94].

Usually, the number densities ( $\rho$ ) or the surface excesses ( $\Gamma$ ) for the ions and water molecules are normalized concerning the corresponding bulk values where surface excesses are absent. However, in the present study these quantities were expressed in terms of the molality ( $\mu^*$ /mol kg<sup>-1</sup>). To obtain further information about the charge-storage process using the graphite electrode in different electrolytes, in the presence of an applied surface charge density to the carbon atoms present in the graphite layers, classical Molecular Dynamics (MD) simulations for three aqueous electrolytes were carried out (*e.g.*, 1.0 mol kg<sup>-1</sup> Li<sub>2</sub>SO<sub>4</sub>, 1.0 mol kg<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>, and 0.5 mol kg<sup>-1</sup> K<sub>2</sub>SO<sub>4</sub>). The Madrid-2019 nonpolarizable force field was applied [52]. This force field is based on scaled charges to prevent the unphysical association observed for aqueous salt solutions with nonpolarizable force fields for concentrations below the experimental solubility [95].

Despite some authors recently recommended the use of the constant potential method (CPM) instead of the less time-consuming simulation approach based on the fixed charge method (FCM) [85,96], significant differences in these cases are only observed for considerable potential differences (*e.g.*,  $\Delta \Psi > 4.0$  V) or high surface charge densities (*e.g.*,  $\sigma S \ge 0.74$  e nm–2). As discussed by Wang *et al.* [86], at low potential differences (*e.g.*,  $\Delta \Psi \le 2.0$  V), most common aqueous electrolytes, the FCM and CPM methods yield the same theoretical findings.

The theoretical findings are summarized in **Figure 8 and 9**. As shown in the snapshots of **Figure 8**(a-c), the ions are clearly disaggregated. **Figure 9**(a-c) shows the normalized density distribution along with the radial distance ( $\mu^*(x)$ ) for the different monovalent cations as a function of the applied surface charge density ( $\sigma/\mu C \text{ cm}^{-2}$ ). The molality normalization was calculated based on the bulk value (*e.g.*, 25–55 Å). In **Figure 9**(a-c), an enhancement in the cation density distribution from 0 up to -9.700  $\mu C \text{ cm}^{-2}$  for Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup> is observed. This is more evident for K<sup>+</sup> cations, since this cation is larger compared to Li<sup>+</sup> and Na<sup>+</sup>, and consequently, less hydrated. Therefore, it is expected higher cation density distribution values for K<sup>+</sup> cations (Please see further discussion). By integrating the local normalized density distribution accounting for the first adsorbed layer, one can calculate the local value of the cationic molality ( $\mu^*$ ).



**Figure 8**. Snapshots from molecular dynamics simulation of the systems at neutral charge: (a)  $Li_2SO_4$  1.0 M, (b)  $Na_2SO_4$  1.0 M, and (c)  $K_2SO_4$  0.5 M. Atom color code: lithium – magenta, sodium – cyan, potassium – purple, sulfur – yellow, oxygen – red, water – light gray, and graphite – dark gray.

The distribution in **Figure 9** for the different cations located in the ~ 0.25 to 0.45 nm range represents the surface excess ( $\Gamma$ ) of the ionic species incurred by the coulombic interactions with the charged (polarized) graphene layers. Since the water is present at high concentrations of ~ 56 mol dm<sup>-3</sup>, a negligible influence of the cationic species on the water surface excess is verified (data not shown). In addition, one has a high water surface excess confined in the 0.3–0.45 nm range followed by another small surface excess centered around ~ 0.6 nm. As expected for concentrated ionic solutions, it was verified in the present study an average EDL thickness for the compact Helmholtz layer of ~ 1.0 nm.

The formation of the *oriented water dipole layer* (WDL) in the inner Helmholtz layer (IHL) is an important phenomenon ascribed to the interruption of the continuous hydrogenbonding network formed in the bulk phase by the solid hydrophobic graphite surface. Commonly, the width of WDL, which exhibits a very low dielectric constant of  $\varepsilon_{WDL} = 6$ , is  $d_{WDL} \sim 0.3$  nm [42]. The small values for these parameters result in compensating effects for the overall capacitance since  $C_{\rm H} \propto \varepsilon_{WDL}/d_{WDL}$ , *i.e.*, if the normal bulk properties ( $\varepsilon_{\rm bulk} \sim 80$  at 298 K) were verified for the IHL the overall capacitance would probably be controlled by the diffuse double-layer capacitance ( $C_{\rm GC}$ ) even for concentrated electrolytes. This behavior is in agreement with the pioneering work by Booth [97], who presented an extension of the Onsager and Kirkwood theories of polar dielectrics to consider the dielectric constant at the high field strengths present in the EDL structures. The important issue regarding the influence of the dipole orientation on the EDL properties was extensively investigated from the theoretical viewpoint by Böckris, Devanathan, and Müller [98]. Modern EDL models based on the improvement or modifications of the earlier ones were proposed and reviewed by Schmickler and Henderson [99], among others [69,100–110].



**Figure 9.** Normalized density distribution along z direction for: (a) Li<sup>+</sup>, (b) Na<sup>+</sup> and (c) K<sup>+</sup> with applied surface charge.

The different regions containing the surface excesses in the compact Helmholtz layer (HL) were designated by Grahame as the '*inner*' and '*outer*' regions to account for the specifically adsorbed species that invades the WDL to enter in intimate contact with the electrode material [102]. Several experimental findings revealed that the Helmholtz layer is unaffected by the electrolyte concentration and/or the thermal effects [79]. The theoretical behavior exhibited by the compact HL was studied by different authors using distinct simulations methods [89,111–113].

The excess surface profiles are different for the distinct monovalent cations (**Figure 9**). The WDL hinders the hydrated cations from moving directly onto the graphene surface, resulting in the first surface excess practically overlapped with the WDL located in the IHP. Recent studies revealed that in the absence of specifically adsorbed anions, the formation of the first surface ionic excess can arise from distortions of large-sized cation's hydration shell in the presence of a strong electrical field [89]. The less pronounced surface excess located at 0.55 - 0.75 nm interval comprises the formation of the OHP.

Even in the absence of an applied surface charge density to the carbon atoms of the graphene sheets, the IHP and OHP regions are clearly verified in the different simulations accomplished for the different monovalent cations. However, the intensities order for the ionic surface excess referring to the IHP are  $\Gamma(\text{Li}^+) >> \Gamma(\text{Na}^+) >> \Gamma(\text{K}^+)$ , while one has for the other ionic surface excess referring to the OHP that  $\Gamma(\text{Li}^+) > \Gamma(\text{Na}^+) \sim \Gamma(\text{K}^+)$ . These findings indicate extreme penetration of the Li<sup>+</sup>-species into the Helmholtz layer compared to the other monovalent ions, *i.e.*, the Li<sup>+</sup> ions showed a higher specific affinity to the graphene electrode. The presence of oscillations in **Figure 9** exhibited by the surface excesses in terms of the molality ( $\mu$ ) indicates some differences concerning the classic Gouy-Chapman-Stern (GCS) model where the surface excess is expected to continuously decrease with the distance. Thus, the present findings indicate that the first ionic excess in intimate contact with the WDL contains more opposite charges than the total electronic charge present in the graphene layer. Similar findings were previously reported by Jiang *et al.* [89].

The inherent theoretical difficulties regarding the analysis of the WDL region and the specific adsorption phenomenon were implicit in the work by Nagy *et al.*[42]. In brief, these authors verified that the G-C diffuse layer properties depend on the lower dielectric constant in the compact Helmholtz layer, which is commonly assumed in several cases using Poisson's equation.
#### 2.3.3.2. Theoretical analysis of the Raman using the MD simulations

It is well-known from earlier studies [77] that the spectral changes verified for the graphite electrodes in the *in-situ* (*operando*) Raman experiments are associated with the phase transitions during the ionic species intercalation between the first graphene layers accessible by the electrolyte. For instance, the cations electrochemical intercalation can be assessed using Raman spectroscopy by measuring the graphite different stage index (*n*), *i.e.*, the number of graphene layers between adjacent intercalate layers. The relative intensities of the Raman doublet (*R*) on the stage index are given by the relation [114] R = k[(n-2)/2], where n > 2 and k is the constant ratio of the cross-section for Raman scattering from the interior (E<sub>2g2</sub><sup>(*i*)</sup>) and bonding (E<sub>2g2</sub><sup>(*b*)</sup>) layer modes, commonly measured with a laser penetration depth of *ca*. 100 nm.

Therefore, we consider in this work that the Raman shift observed for the D-peak is due to the cation insertion between the first graphene layers composing the graphite structure. In this sense, we used as the theoretical model a symmetric box filled with the different electrolytes whose walls were composed of evenly spaced graphene layers to originate mesoscopic slit pores in the graphite structure. In light of these considerations, we propose that the shift in the D-peak position ( $\omega$ ) as a function of the surface potential ( $\Psi$ ) incurred by the applied surface charge density ( $\sigma$ ) proportional to changes in the surface cationic concentration ( $\mu^*$ ) according to the following relationship:

$$\frac{\partial \omega}{\partial \Psi} = \alpha \, \frac{\partial \mu^*}{\partial \sigma} \tag{4}$$

Applying the chain rule on the right-hand side of Equation (4), we obtain the Equation (5):

$$\frac{\partial \omega}{\partial \Psi} = \alpha \, \frac{\partial \Psi}{\partial \sigma} \, \frac{\partial \mu^*}{\partial \Psi} \tag{5}$$

Thus, one might rewrite the Equation (5) as follows:

$$\frac{\partial \omega}{\partial \Psi} = \alpha' \frac{\partial \mu^*}{\partial \Psi},\tag{6}$$

where:

$$\alpha' = \alpha \frac{\partial \Psi}{\partial \sigma} \tag{7}$$

Assuming that  $\alpha'$  remains constant for the different applied surface charge densities, one can integrate the Equation (6) to obtain the following expression:

$$\Delta \omega = \alpha' \Delta \mu^* \tag{8}$$

**Figure 10**(a-c) compares experimental and calculated Raman shifts as a function of the surface potential. A good agreement between the experimental results and the correlated values was obtained using the Equation (8). The fitted values for  $\alpha'$ , however, are different for each electrolyte (*e.g.*, 0.33 for Li<sub>2</sub>SO<sub>4</sub>, 1.0 for Na<sub>2</sub>SO<sub>4</sub>, and 0.16 for K<sub>2</sub>SO<sub>4</sub>). In principle, these findings indicate the different hydrated cations with distinct volumetric charge densities results in different degrees of insertion regarding the first graphene layers of graphite.



**Figure 10.** Comparison between experimental and calculated Raman frequency shifts for (a)  $1.0 \text{ mol } \text{kg}^{-1} \text{ Li}_2\text{SO}_4$ , (b)  $1.0 \text{ mol } \text{kg}^{-1} \text{ Na}_2\text{SO}_4$ , and (c)  $0.5 \text{ mol } \text{kg}^{-1} \text{ K}_2\text{SO}_4$  aqueous solutions. Solid and open symbols in the graphs correspond to experimental and simulated data, respectively.

It was proposed here that the preferential charge concentration on the surface affects the charge mobility between the first graphene layers of graphite. Even if the charge adsorption energy is close to the work function, it is insufficient to extract electrons. Thus, the scattered photon that comes out to the system is changed because there is an electrolyte charge concentration that can trap charges and change the graphite surface. Even though the simulation results here aimed to represent just the carbon surface with the ions present, the excellent correlation for the D-peak shift may also imply that a similar charge trapping due to the solvated inserted cations interaction to the graphite, are causing a similar consequence for the Raman signal. From this perspective, if changing the surface potential where the photon reaches, the D-peak has a shift in its position because the displacement of the Fermi level. The present

results corroborate this hypothesis that the cations insertion is entailing changes in the graphite surface, without an appreciable amount of intercalation. Hence, according to our findings, it is possible to draw a conjecture that comprises the cation adsorbed amount, the surface electric potential, and the expected graphite behavior in Raman measurements.

### 2.4. Conclusions

A comprehensive study comprising the *operando* Raman analysis of polycrystalline graphite electrodes under dynamic polarization conditions was accomplished, while molecular dynamics (MD) simulations were provided to elucidate the possible origin of the Raman spectral changes verified for the different aqueous electrolytes containing monovalent cationic species. The experimental electrical double-layer capacitance values determined using different techniques revealed that the present graphite electrode with a rough surface morphology exhibits a very high capacitance compared to the conventional highly oriented pyrolytic graphite (HOPG) electrodes which exhibits a smooth surface morphology. Therefore, the high capacitance values reported above in the redox reaction absence cannot be entirely attributed to the rough/porous nature of the electrode material. Thus, an insertion/extraction mechanism involving the ionic species from the electrolyte must be present to enhance the overall capacitance. In the case of SAPG (or HOPG) electrodes, this type of mechanism is absent due to the compact nature of the pyrolytic carbon material.

Consequently, it proves this higher overall capacitance is not related to electrostatic interaction only, but it is due to the hydrogen sulfate insertion process. It was evidenced a correlation between the reversible Raman D and 2D-band blue-shift and the accumulation/depletion of the different cations at the graphite/electrolyte interface. The reversible blue-shift reduction of the Kohn anomaly on LO phonon branch at the K point during the reversible insertion/extraction of the ionic species. The fundamental processes accounting for this reversible behavior were investigated in light of the theoretical analysis extracted from the MD simulations. A theoretical framework was presented to relate the effect of the applied potential on the Raman D-peak position shift and its correlation to the surface ionic charge. This theoretical approach allowed the calculation of the relative Raman D-peak position shift from the MD simulation results. As a result, it was proposed that the experimentally observed Raman shift is predominantly governed by the graphite-charge interaction with the solvated cation, either at the electrode surface (surface excess) as well from the absorbed solvated cations. Moreover, the present study sheds some light on the charge-storage mechanism of

electrical double-layer capacitors (EDLCs). Our results shine lights on the energy storage processes discussing role of adsorption and insertion at the interface level for supercapacitors.

## Chapter 3

# New insights on the sodium water-insalt electrolyte and carbon electrode interface from electrochemistry and operando Raman studies

### 3.1. Introduction

Supercapacitors (SCs) are energy storage devices with very high specific power and moderate energy. To increase energy densities, it is essential to increase the electrochemical stability of electrolytes and increase the capacitance. For several reasons, there is an interest in replacing the organic electrolytes used in SCs with their less harmful and cheaper aqueous counterpart. This issue is mainly related to the fact that organic-based SCs suffer from low ionic conductivity, flammability, and toxicity [38]. Moreover, for manufacturing procedures, organicbased electrolytes need a high-cost dehumidifier system [115]. By contrast, aqueous-based SCs can offer higher specific capacitance, higher ionic conductivity, lower resistance, and even most important, there is no need for special manufacturing procedures, which strongly simplify the large-scale production process [116]. On the other hand, the reduced electrochemical stability window (ESW) of 1.23 V is a drawback for using the aqueous-based electrolytes in practical devices since the stored energy scales with the voltage ( $E = CU^2/2$ ), where C represents capacitance, and U is the WVW of the cell [8,34]. In this sense, researchers from different countries have suggested that aqueous electrolytes obtained from highly concentrated solutions can widen the ESW of SCs [117-126] since the great excess of salt ions can form the solvent blocking interface (SBI), which can affect the water-splitting initially predicted at 1.23 V vs. SHE due to a combination of thermodynamic and kinetic effects in the positive electrode [120]. In the positive electrode, a hypothesis of steric and hydrophobic effect is shown. At negative electrodes, Suo et al. [118] hypothesize the TFSI reduction; Dubouis et al. [127] hypothesize the film layer formation by the indirect attack of TFSI, and Bouchal *et al.* [128] gives the argument of salt precipitation due to electrolyte close to saturation. For all cases, the cation of the salt is generally an element of the first column of the periodic table, which means there are not a big cation.

From thermodynamics, the *equilibrium cell voltage* for water-splitting is affected by the *ionic strength* (the effective electrolyte concentration) since the latter governs the *partial pressure* of the dissolved gases (salting-out effect), *i.e.*, when  $P(O_2)$  and/or  $P(H_2)$  inside the coin cell is lower than 1.0 bar, the equilibrium voltage is decreased from 1.23 V *vs*. SHE [129,130]. At the same time, from the kinetic viewpoint, the presence of *dissipative effects* due to an activation overpotential (Butler-Volmer's model) for the electron transfer push the minimum voltage for water-splitting to more positive values in relation to the rest condition [131]. In this sense, the overpotential for water-splitting is increased at higher electrolyte concentrations since the structure of the activation barrier is affected, decreasing the chemical activity of the reaction intermediates in the compact (Helmholtz) region of the electrical doublelayer. Therefore, the influence of the electrolyte concentration on the verified ESW in SCs is composed of thermodynamic and kinetic effects.

From the above considerations, the last decade has witnessed several attempts to understand the so-called *water-in-salt electrolyte* (WiSE) behavior [117–126,132]. Suo and co-workers emphasized that WiSE systems are electrolytes where salt particles outnumber the solvent in weight and volume [118].

However, due to a lack of fundamental information in the recent literature, this work presents some important concepts regarding the *normal* and *potential* (WiSE) electrolytic solutions and some implications in the study of aqueous-based SCs. It worth mentioning that from the fundamental viewpoint, the *water-in-salt* concept applies for every electrolytic solution where the number of the *dissociated ionic species* is so high that aqueous electrolytes no longer obeys the Debye-Hückel or Davies equations representing '*true electrolyte solutions*' [133]. In this sense, WiSE systems are *abnormal electrolyte solutions* since their thermodynamic properties cannot be theoretically predicted using particular models for the *activity coefficient* ( $\gamma_{\pm}$ ) of the dissolved ionic species. For normal electrolyte solutions ( $\approx$ 0.001–0.1 *m*), one can calculate the extra free energy ( $\Delta_{ext}G$ ) of an ionic species due to electrostatic repulsions and attractions involving the other ions [134,135].

Normal electrolyte solutions contain a negligible amount of "ion pairs," which are the dissolved *but undissociated* ionic species (*e.g.*,  $NaClO_{4(aq.)}$ ) resulting from *very strong* 

*electrostatic repulsions* formed at short-separation distances ( $d \approx 0.35$  nm). This important concept incorporated in *The Theory of Ion Pairs* was proposed by Bjerrum [136]. These considerations are implicit in different modern computer (MD & Monte Carlo) simulations involving the properties of the electrolytic solutions. The formation of "short-range ion pairs" in normal electrolytes is not considered in the Debye-Hückel and Davies models. However, the extent of ion-pair formation dictates the value of the *real ionic concentration* used in the "ionic-cloud model" representing the behavior of different electrolytes. Therefore, there is a vital distinction between "*normal*" and "*potential (apparent*)" electrolytes that is not commonly considered in the recent literature.

On the basis of the above-mentioned considerations, WiSE systems belong to the latter case (potential electrolytes), where *only a fraction* of the molal (*m*) concentration,  $(1 - \theta) \times m$ , is in the *true ionic state* (*e.g.*, Na<sup>+</sup><sub>(aq.)</sub> and ClO<sub>4<sup>-</sup>(aq.)</sub>). The remaining fraction,  $\theta \times m$ , is found in the *undissociated ionic state* (*e.g.*, NaClO<sub>4(aq.)</sub>), similar to a non-polar substance dissolved in the aqueous medium. Therefore, in WiSEs, the  $\theta \times m$ -fraction imposes in the compact (Helmholtz) region of the electrical double-layer (EDL) a great substitution of the *oriented water dipoles* by *undissociated ionic species* (ion pairs) resulting in different electrical properties (*e.g.*, intrinsic conductance, dielectric constant, etc.). As a result, the electrode/solution interface can exhibit an abnormal behavior regarding the ESW and the activation barrier for electron transfer during water-splitting compared to a *normal electrolyte* containing the same ionic species. In addition, when a high electric field is applied during polarization, the different surface excesses ( $\Gamma_{w-dipoles}$ ,  $\Gamma_{anion}$ , and  $\Gamma_{ion-pair}$ ) are changed, and *local precipitation* of the solute (*e.g.*, NaClO<sub>4(s)</sub>) can occur due to expulsion of water dipoles (the solvent species) from the interface ( $\Gamma_{cation} / \Gamma_{anion} \gg \Gamma_{w-dipoles}$ ) incurred by the strong electrostatic interactions [137].

As a result, one has the formation of a *solvent blocking interface* (SBI) or, more precisely, in a *saturated blocking interface*. Unfortunately, this type of analysis based on well-established theoretical foundations is rarely found in the literature dealing with WiSEs used in ideal electrodes. It is worth mentioning that in NaClO<sub>4</sub> solutions, the amount of dissolved salt overcomes the water molecules in terms of the partial molar properties (mass and volume) for a concentration of *ca*. 8.17 *m* [118]. Therefore, an abnormal electrochemical behavior is expected to occur in the current work using concentrated solutions (*e.g.*, 17 *m*).

In addition to the fact that it permits a larger ESW while ensuring less toxic or nonflammable conditions, the highly-concentrated electrolytes are usually reported in the literature using  $Li^+$  and  $Na^+$  ionic species [117–126]. Unlike the commonly used electrolytes based on  $Li^+$ -ions found only in some countries (*e.g.*, Chile), Na<sup>+</sup>-based electrolytes are quite interesting because sodium is abundantly found in nature, making it more economically competitive while enabling the development of local supply chains in different countries.

Most WiSE-based literature reports are concerned with the super-concentrated LiTFSI electrolyte system. In this case, some studies reported different concentration and ESW values (e.g., 20 m & ~2.4 V [124], 21 m & 2.6–3.0 V [122,125] and 31 m & 2.4 V [126]). On the other hand, some authors [138–141] reported that NaClO<sub>4</sub>-based WiSE systems exhibit better performance at 17 m & 2.3–2.8 V. These WiSEs resulted in voltage windows similar to those commonly verified for the less friendly, more toxic, hard to handle, and flammable organicbased electrolytes. In addition, it was verified in some cases the use of the composite organic solvents, such as those containing 21 m LiTFSI/H<sub>2</sub>O/ACN with a ESW of 2.4 V [119] and 8 m NaClO<sub>4</sub>/(H<sub>2</sub>O)<sub>1.5</sub>(AN)<sub>2.4</sub> with a ESW ~2.5 V [117]. Some SCs that operate using high ESW has the drawback of presenting low specific energy retention after the cyclability tests, thus resulting in considerable energy losses, *i.e.*, 85% (2.5 V/5,000 cycles) [117], 95% (2.6 V/7,000 cycles) [125]. 80% (2.3 V/10,000 cycles) [138], and 80% (2.4 V/40,000 cycles) [119]. In principle, this moderate energy retention exhibited by WiSE-based SCs seems to indicate that these devices are operating under water-splitting conditions, which considerably reduces the overall performance of the device and its chemical and mechanical stabilities. Unfortunately, no information about this crucial issue was provided in the aforementioned studies.

The reasoning about that indicates that the verified losses in the NaClO<sub>4</sub>-based WiSE systems can be due to the occurrence of the water-splitting process with a small leakage (background) current across the *electrical double-layer* (EDL) structure. In general, this small faradaic current ( $I_f$ ) in SCs is difficult to detect using solely the conventional *cyclic voltammetry* (CV) and *galvanostatic charge-discharge* (GCD) techniques due to the pronounced contribution of the capacitive current ( $I_c$ ), where  $I_{overall} = I_c + I_f$ . Commonly, one has at high scan rates that  $I_c >> I_f$  resulting in  $I_{overall} \approx I_c$ . In this sense, the use of *single-step chronoamperometry* (SS-CA) and *electrochemical impedance spectroscopy* (EIS) techniques can be quite helpful to identify the ESW in SCs correctly. Nunes *et al.* [142] reported very accurate findings showing excellent internal consistency regarding the different electrochemical techniques could permit the identification of the ESW unambiguously. Unfortunately, several authors have tried to establish the ESW in WiSEs considering only the

CV findings at high scan rates and/or GCD using high gravimetric currents, which mask the irreversible faradaic (water-splitting) reaction.

From these considerations, it was investigated in the present work the real ESW-values for the NaClO<sub>4</sub>-based WiSEs using a rational experimental approach comprising the combination of three different electrochemical techniques. Another recent development in the study of energy storage devices is based on the *operando* (*in-situ*) experimental approach where an external radiation source impinges the electrode material during the static or dynamic polarization of the electrode/solution interface. In this way, *operando* analyses using spectroscopy coupled to electrochemical techniques shed light on understanding the fundamental processes governing the charge-storage mechanism in SCs [21,23–36]. These analyses have been accomplished by several prominent authors for different energy storage materials [8,27,143,144]. A very interesting example of a spectroscopic approach used in the *operando* analyses is based on the Raman technique, which can reveal during the cell polarization and/or the solid-state redox processes [145].

Graphite, formed from pilled-up graphene layers weakly connected by van der Waals interactions generated by delocalized *p*-orbitals [146] is an excellent model to access these fundamental processes. Because of the graphite anisotropy characteristics, electrolyte species could insert between its layers, causing charge-transfer reactions, which form the so-called intercalation phenomena. The adsorption/physical process and ionic intercalation/chemical process both can be observed through changes in Raman spectra of carbon-based electrodes under *polarization conditions*, *i.e.*, *operando* Raman studies [21,147]. The Raman spectra of the ionic species intercalating between the graphite layers are assigned by the doublet structure formed close to the high-frequency phonon  $E_{2g1}$  corresponding to the G-band. The presence of ionic species changes the environment, causing a reorganization of graphite [114]. Likewise, the ionic adsorption/desorption processes affect the position (wavenumber) of the defect-induced D-band changes. The latter is a function of the Fermi energy variations around the *K* and *K'* points present in the Brillouin zone [13,148].

The intercalation of  $ClO_4^-$  species into graphite electrodes was previously reported by Gao *et al.* [149]. However, this study was carried out only in organic electrolytes. In this sense, many physicochemical characteristics of the NaClO<sub>4</sub>-based WiSE system, including the best ESW conditions in aqueous solutions, can be better understood in the present work with the aid

of the *operando* Raman analysis. To the best of our knowledge, the accomplishment of Raman *operando* studies comprising devices under WiSE conditions is practically absent in the literature. Generally, the *operando* Raman technique has only been applied to electrochemical systems composed of normal electrolytes (*e.g.*, low and moderate concentrations) using organic solvents [23–34].



**Figure 11.** Scheme showing the *operando* Raman studies performed under dynamic voltage conditions. In the dynamic case, CV experiments were used, and the D-band's reversible shifts are detected as a function of the electrolyte concentration (molal unities). On the other hand, at constant (static) voltage conditions, the SS-CA experiments involving G-band splitting are typical of ionic intercalation.

Compared to other WiSEs, the highly-concentrated NaClO<sub>4</sub> solutions have excellent solubility, low viscosity, and high conductivity [117,150]. From these considerations, the current work uses different NaClO<sub>4</sub> concentrations for applying the good practices recently proposed to identify the ESW in SCs correctly [142]. Subsequently, *operando* Raman studies were performed for different NaClO<sub>4</sub> concentrations using dynamic (CV) and static voltage (SS-CA) conditions, as summarized in **Figure 11**. As seen, the advantages of using the Raman

spectroscopy together with electrochemical methods are the following: (*i*) CV case, one might see the D-band shifts indicating a reversible anion insertion process in the host electrode material, and (*ii*) CA case, it was verified an irreversible ionic intercalation process, *i.e.*, a process affecting the  $E_{2G}$  and  $E_{2G}$ '-bands. As a result, an in-depth understanding of the charging mechanism occurring at the electrode/solution interface can be achieved in the presence of WiSE systems.

In the current work, the WiSE concept was used for studying the physicochemical behavior of SCs to address different issues concerned with the expansion of the ESW in different highly concentrated NaClO<sub>4</sub> aqueous solutions. Activated carbon is the 'standard material' for commercial SCs. However, this material imposes some difficulties in accomplishing the spectroscopic and some electrochemical studies due to its porous nature with complex surface morphology. Therefore, this work uses a polished commercial graphite pressrod electrode as a 'model carbon-based material'. With that in mind, it is possible to access the adsorption/desorption and intercalation processes with *operando* Raman (static and dynamic polarization conditions) simultaneously. In particular, this study addressed the influence of WiSE concentration on the ESW and the behavior of the charge-storage process occurring at the electrode/electrolyte interface, *i.e.*, where the electrolyte properties strongly affect the electrical double-layer characteristics, including the short-range carbon-ion interactions.

### 3.2. Experimental

#### **3.2.1. Electrode preparation**

A graphite billet with a 1.6 cm diameter from the MG2 graphite from CM Carbon Co. (China) was cut into pieces with a 0.1 cm thickness. After this process, the electrodes were polished using the #400 to 1200 grit emery papers and finalized with  $Al_2O_3$  in a metallographic polishing cloth (See **Figure S4(a)**). For use in the *operando* Raman studies, the upper (counter) electrode received a hole with a 0.2 cm diameter for the laser to reach the *working electrode* (WE) surface.

#### 3.2.2. Operando Raman measurements

The spectra were taken at 60 s with 1 accumulation during the CV tests at 1 mV s<sup>-1</sup> and 55 s with 1 accumulation for the SS-CA tests of 5 min. The equipment used was a Renishaw Raman Spectrometer equipped with different lasers (*e.g.*, 785 and 514 nm). **Figure S4 (b & c)** shows the photos of the *operando* Raman experimental setup. Also, **Figure S4 (d)** presents the images taken on the electrode region where the laser impinged the surface just before the *operando* Raman experiments accomplished for each electrolyte concentration (1, 5, 10, and 17 *m*).

#### **3.2.2. Electrochemical measurements**

CV, EIS, SS-CA, and GCD experiments at room temperature (24°C) were performed using a two-electrode cell configuration. A model VersaSTAT 4 potentiostat-galvanostat from Ametek was used throughout.

Areal capacitances were calculated from the GCD discharge (negative slope) using the following equation:

$$C_{\text{areal}} = \frac{I}{A\left(\frac{dU}{dt}\right)},\tag{9}$$

where *I* is the discharge (cathodic) current, *A* is the area of both electrodes, *U* is voltage and dU/dt is the slope of the discharge curve.

The specific energy was obtained by **Equation 10**:

$$E = \frac{CU^2}{2h} \left(\frac{10^3}{3600}\right),\tag{10}$$

where *h* is the cell height.

The specific power was calculated using the **Equation 11**:

$$P = \frac{E}{t} \tag{11}$$

where *t* is the discharge time and *E* is the specific energy.

The real and imaginary parts of the complex capacitance were calculated from the impedance data using the following equations:

$$C(\omega) = C'(\omega) - jC''(\omega), \qquad (12)$$

where

$$C'(\omega) = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2},$$
(13)

$$C^{\prime\prime}(\omega) = \frac{Z^{\prime}(\omega)}{\omega |Z(\omega)|^2},$$
(14)

### 3.3. Results and Discussion

# **3.3.1.** Electrochemical approach to determine the ESW for WiSE-based SCs

**Figure 12** shows the electrochemical findings obtained using CV, EIS, and SS-CA to correctly identify, using the graphite electrode, the ESW unambiguously as a function of the NaClO<sub>4</sub> concentration. The comparative analysis in this study regarding the different experimental data is of great relevance for practical purposes. The limitations of the CV technique commonly used alone to discriminate between capacitive and faradaic currents can be circumvented. It was verified an excellent internal consistency between the EIS and SS-CA findings used in association to detect the onset of the water-splitting reaction.

As can be seen, the use of EIS (*e.g.*, a frequency-dependent test) and SS-CA (*e.g.*, a stationary voltage test) permits a rational choice regarding the cut-off voltage as a function of the electrolyte concentration, which can be then used in the conventional CV and GCD experiments to obtain the figures-of-merit representing the overall electrochemical performance of SCs. **Figure 12** highlights the influence of the different NaClO<sub>4</sub> molal concentrations (*e.g.*, 1 *m*, 5 *m*, 10 *m*, and 17 *m*) showing in the left panel the CV at 1 mV s<sup>-1</sup> for different *anodic vertex voltages* (AVVs), *i.e.*, the positive voltage limits for the scan rate reversal.

For each AVV value, EIS and SS-CA experiments were carried out to verify the capacitive response expected for well-behaved EDLCs. In the absence of parasitic (faradaic) reactions, the impedance data must be characterized by an almost vertical line ( $\varphi \approx -90^\circ$ ) at

low frequencies in the complex-plane plot. Considering the constant phase element (CPE) approach, used in the case of real (solid) electrodes, due to the frequency dispersion phenomenon, the imaginary part of the impedance ( $Z_{(Im)} = Z_{cpe}$ ) of the *blocked electrode* (SCs) at low frequencies (*e.g.*, *f* < 10 Hz), after incorporation of the Brug-Sluyters formula, can be represented by the following linearized equation:

$$\ln(Z_{\rm CPE}) = -C_{\rm EDL}^{(n)} \times \left(\frac{1}{R_{\rm ESR}}\right)^{(n-1)} - n \times \ln(2\pi f), \qquad (7)$$

At the same time, in the case of SS-CA (single-step voltage experiments), the currenttime (transient) plot must be an exponential decay for a blocked (capacitive) interface, *i.e.*, the measured currents must fade away (*e.g.*,  $I/I_0 \le 0.01$ ) at short polarization times (*e.g.*,  $\approx 0.1-10$ s). This behavior is predicted by the  $I = I_0 \times \exp(-t/\tau)$  relationship, where  $\tau$  is the system's time constant ( $\tau = R_{\text{ESR}}C_{\text{EDL}}$ ). Therefore, an almost constant current in SS-CA experiments denounces the parasitic (faradaic) current due to water-splitting.

As can be seen, the CV plots in **Figure 12** suggest that high electrolyte concentrations increase the ESW. Liumin Suo *et al.* [120] suggested that this increase occurs due to the formation of a *solvent blocking interface* (SBI), which hinders the water-splitting suppressing the gas evolution during the charge-discharge processes, *i.e.*, the almost-free oriented dipoles commonly present in the inner Helmholtz plane of the *electrical double layer* (EDL) structure is partially replaced by water dipoles tightly attached to the solvation shells of the different electrolyte ionic species. As a result, water's *chemical activity* at the interface is drastically decreased due to their involvement in the solvation processes, resulting in a reduced amount of the H<sub>2</sub>O as free molecules to undergo electrolysis (Please, see further discussion).



**Figure 12.** Electrochemical data for the graphite electrode using different NaClO<sub>4</sub> electrolytes: (**a-c**) 1 *m*, (**d-f**) 5 *m*, (**g-i**) 10 *m*, and (**j-l**) 17 *m*. The different techniques (CV, EIS, and SS-CA) to identify the ESW in SCs correctly. Scan rate: 1 mV s<sup>-1</sup>. Frequency range: 10 kHz to 10 mHz.

Firstly, one might highlight the high ESWs obtained for the 10 *m* & 17 *m* solutions at ~1.6 V (**Figure 12(g**)) and ~1.8 V (**Figure 12(j**)), respectively. However, a close inspection of these findings revealed the presence of a current increasing indicating the onset of the irreversible gas-evolving water-splitting reaction occurring below 2 V. In other words, the current increasing corresponds to the voltage region where there is a faradaic contribution of water-splitting to the overall voltammetric current. The 'red circle' in the inset of **Figure 12(a)** evidences the current increasing. This behavior is theoretically predicted by the well-known Butler-Volmer's reaction model where the faradaic current exponentially increases with the voltage. For an ideal EDLC in the presence of equivalent series resistance ( $R_{ESR}$ ), the capacitive voltammetric *current-voltage* response is *almost rectangular* according to **Equation 15**:

$$I_{\rm C} = C_{\rm EDL} \nu \left[ 1 - \exp\left(\frac{-\Delta U}{R_{\rm ESR} C_{\rm EDL} \nu}\right) \right],\tag{15}$$

On the contrary, in the presence of a faradaic process (*e.g.*, water-splitting), the voltammetric profile shows an upward/downward curved border for the anodic/cathodic scans, respectively. Considering the *anodic* (positive) voltage scan, the overall current (*I*) in the presence of the irreversible *oxygen evolution reaction* (OER), under high-field approximation conditions (*e.g.*,  $U-U_{0(OER)} \ge 70$  mV), is given by the following relationship:

$$I = I_{\rm C} + I_{\rm F} = C_{\rm EDL} \nu \left[ 1 - \exp\left(\frac{-\Delta U}{R_{\rm ESR} C_{\rm EDL} \nu}\right) \right] + I_{0(a)} \exp\left[\frac{\alpha_{\rm a} F\left(U - U_{0(\rm OER)}\right)}{RT}\right],\tag{16}$$

where  $I_{0(a)}$  is the anodic exchange current density measured at  $U = U_{0(OER)}$ ,  $\alpha_a$  is the anodic charge-transfer coefficient, *R* is the universal gas constant, and *T* is the absolute temperature.

Accordingly, the cathodic (negative) voltage scan counterpart of the voltammetric curve  $(e.g., |U-U_{0(\text{HER})}| \le 70 \text{ mV})$  for the reversal process ( $\nu < 0$ ) can be represented by **Equation 17**:

$$-I = I_c + I_f = -C_{\text{EDL}} \nu \left[ 1 - \exp\left(\frac{\Delta U}{R_{\text{ESR}} C_{\text{EDL}} \nu}\right) \right] - I_{0(c)} \exp\left[\frac{-\alpha_c F\left(U - U_{0(\text{HER})}\right)}{RT}\right], \quad (17)$$

where  $I_{0(c)}$  is the cathodic exchange current density measured at  $U = U_{0(\text{HER})}$ , and  $\alpha_c$  is the cathodic charge-transfer coefficient.

Equations 15 and 16 represent the typical "mirror-like" voltammetric curves ( $I_c = \pm Cv$ ) with current plateau (*rectangular profile*) when  $R_{ESR} \rightarrow 0$ ,  $|U-U_0| \approx 0$  (or  $I_0 \approx 0$ ), *i.e.*, the voltammetric response is characterized by a symmetry between the anodic and cathodic branches. On the contrary, with superimposed faradaic components ( $|U-U_0| > 0$  and  $I_0 > 0$ ), the VCs are characterized by current increasing close to the vertex voltages. Therefore, in the

absence of water-splitting (*e.g.*, OER & HER), only the first terms in **Equations 15 and 16** survive. In addition, when  $R_{\text{ESR}} \rightarrow 0$ , one has a *perfect rectangular* capacitive voltammetric profile expected for EDLCs where the anodic and cathodic current plateaux are  $I_a = Cv$  and  $-I_c = -Cv$ , respectively.

From the above theoretical considerations, the influence of WiSEs on the ESW is due to changes in the kinetic parameters (*e.g.*,  $I_0$  and  $\alpha$ ) caused by modifications in the EDL structure, especially in the compact Helmholtz region. Generally, a high surface excess of the ionic species ( $\Gamma_{\text{ions}}$ ) strongly solvated in their hydration shells decreases the charge flow across the EDL, decreasing the influence of the applied overvoltage on faradaic currents. As a result, the ESW can be expanded in the presence of WiSEs in comparison to *normal electrolytes*.

The analysis of **Equations 15 and 16** shows that high scan rates ( $\nu$ ) promote a considerable increase in the capacitive current in relation to the faradaic component. As a result, the presence of water-splitting in the VCs can be drastically masked, *i.e.*, the current is partially wasted in water-splitting, thus causing a cell precocious failure with no real gain in energy storage. Although several works reported *quasi-rectangular* VCs as proof of well-succeeded devices, in practice, we do not usually apply energy storage devices as in the manner of a CV-like experiment. Instead, it is of everyday use the galvanostatic discharge with different cutoff voltages and current densities. In addition, the energy equation,  $E = \frac{1}{2} CU^2$ , gives us a first impression that by widening the cell voltage (U), we may have great improvement in the stored energy. However, suppose the electrochemical device is sustaining a water-splitting. In that case, the *U*-value does no longer hold at the open-circuit voltage in a pre-charged device as occurs for well-behaved SCs. In other words, it isn't easy to obtain meaningful findings using high scan rates and widening the ESW without the auxiliary use of the SS-CA and EIS techniques.

Unfortunately, most literature reports regarding the use of highly-concentrated electrolytes have applied the CV technique alone using relatively high scan rates (*e.g.*,  $\nu > 50$  mV s<sup>-1</sup>) to define the ESWs. Through a comparison using scan rates of 10 and 100 mV s<sup>-1</sup> (**Figure S1(a-h**) – Supporting Information), it was noticed that high scan rates could drastically mask the presence of faradaic currents due to water-splitting, which can be properly identified by the presence of an anodic current increasing at 1 mV s<sup>-1</sup> (**Figure 12**). Thus, the ESW that appeared to be 0.8 V at 10 mV s<sup>-1</sup> at 1 *m* then dropped to 0.6 V at 1 mV s<sup>-1</sup>. Apparently, in the case of a 5 *m* solution, it could be easy to reach ESWs of up to 1.4–1.6 V. However, the voltage value must be 1.4 V considering the lower scan rate data. For a 10 *m* solution, the ESW dropped

from 1.8 V to 1.6 V (1 mV s<sup>-1</sup>). Lastly, in the case of the 17 *m* WiSE system, according to the literature [138–141], it could be observed high ESWs of *ca*. 2.0–2.2 V. However, a close inspection of our VCs indicates an anodic current increasing above 1.8 V (**Figure 12(j**)).

For a more accurate analysis of the ESW, the use of EIS is necessary. In this sense, the complex-plane plots showed in the second panel of **Figure 12** contain information useful for identifying the capacitive voltage intervals in WiSEs. In short, the presence of a parasitic irreversible faradaic (*e.g.*, electrolyte decomposition) reaction in EDLCs is characterized in the complex-plane by a poorly developed semicircle. For practical purposes, this behavior translates into a CPE behavior characterized by an exponent (*n*) lower than 0.9 for data collected in the low-frequency range (*e.g.*,  $\approx 10$  Hz to 10 mHz). Also, the correlation coefficient ( $r^2$ ) from the linear regression analysis, using the linearized model (see **Eq. (14**)), is lower than *ca*. 0.998. Thus the combination of n < 0.9 and  $r^2 < 0.998$  comprises an excellent criterion for the correct identification of ESWs, *i.e.*, negligible deviations from the  $R_{\text{ESR}}-C_{\text{EDL}}$  canonic circuit model for EDLCs are then verified. Unfortunately, this rational analysis to discriminate a capacitive behavior using EIS is not commonly considered in the literature.

The complex-plane plots in **Figure 12** show the deviations mentioned above, *i.e.*, at higher voltages and low frequencies, the poorly developed semicircles start to appear (*e.g.*,  $n < 0.9 \& r^2 < 0.998$ ). Our quantitative impedance analysis revealed a ESW of 1.8 V for the 17 *m* NaClO<sub>4</sub> aqueous-based WiSE system, which is lower than those reported in the literature using only the CV technique [138–141]. The current verified ESWs of 0.6, 1.6, and 1.6 V for the 1, 5, and 10 *m* electrolyte concentrations, respectively.

Further experiments using the *single-step chronoamperometry* (SS-CA) technique were accomplished. As seen in the third panel of **Figure 12**, the presence of water-splitting up to voltages 0.6, 1.4, 1.6, and 1.8 V for WiSEs with 1, 5, 10, and 17 *m* concentrations was not verified since the residual currents were negligible after a long polarization time of 240 s. For the upper voltages, the presence of a small parasitic faradaic reaction was verified for these electrolytes. In principle, these findings confirm that the SS-CA technique has a high sensibility for detecting the water electrolysis during the charging process of the electrode/electrolyte interface.

Generally, our comparative study using different electrochemical techniques revealed that the 'model graphite electrode' immersed in concentrated NaClO<sub>4</sub> aqueous-based electrolytes could be used with confidence for the charge-storage process in the absence of



water decomposition considering the ESWs of 0.6, 1.4, 1.6, and 1.8 V referring to 1, 5, 10, and 17 *m* solutions, respectively.

**Figure 13.** Electrochemical data for the model graphite electrode housed in the El-Cell filled with the NaClO<sub>4</sub> electrolytes (1, 5, 10, and 17 *m* solutions). Data extracted from CV (**a-c**), GCD (**d-f**), and floating time (**g-i**) experiments. CV scan rate: 10 mV s<sup>-1</sup>. GCD areal current: 0.05 mA cm<sup>-2</sup>.

**Figure 13** gathers the electrochemical findings considering what has been discussed so far regarding the best ESW for each electrolyte concentration. **Figure 13(a)** shows the linear dependence of the voltammetric capacitive current on the scan rate ( $I_c = Cv$ ), which illustrates the capacitive characteristics for all concentrations. In this approach, the voltammetric currents were measured considering their almost stationary values close to the AVV (**Figure S1(i-I)** – Supporting Information). Generally, the above findings revealed an increase in voltammetric current as a function of the electrolyte concentration. As seen, the device underwent an 18 h of voltage floating time to verify the influence of electrolyte concentration on cyclability (*e.g.*, accelerated cyclability test). In this sense, for each 2 h, five VCs were obtained at 10 mV s<sup>-1</sup> for each electrolyte. Figures 13(b) and 13(c) show the CV data obtained before and after the floating time experiment. Figure 13(d) presents the areal capacitance as a function of the current used in the GCD experiments (Please, see also Figure S1(m-p) - Supplementary Information). The capacitance values were 14.7, 25.5, 16.9, and 25.7 mF cm<sup>-2</sup> for the 1, 5, 10, and 17 *m* solutions, respectively. It was verified high capacitance retentions of 79% and 70% for the 10 *m* and 17 *m* solutions, respectively. These data indicate good charge-storage performance at high electrolyte concentrations (*e.g.*, WiSE conditions).

**Figures 13(e-f)** show some GCD curves at 0.05 mA cm<sup>-2</sup> obtained before and after 18 h of the experiment. Both CV and GCD experiments revealed positive changes after cyclability, indicating improvements in the electrode material's wettability conditions. It is worth noting that the well-known EDLC characteristics (*e.g.*, the almost rectangular VCs and triangular GCDs) were verified for all electrolyte concentrations. **Figure 13(g-i)** shows excellent stabilities verified for all electrolytes regarding the areal capacitance and the specific energy/power as a function of the floating time experiment. In particular, it was verified a 7% capacitance increase for the 5 *m* solution. As discussed, the stored energy in SCs increases with the square of the voltage. Thus, the higher ESW exhibited by the 17 *m* WiSE system yields the best energy and power density values.

**Figure 14(a & b)** presents the long-term cyclability tests using GCD and the best ESW defined through our electrochemical methodology. The capacitance retention of 93.84%, energy retention of 93.75%, and power retention of almost 100% after 160 k cycles prove the excellent functioning of the cell using a true ESW. In comparison with cyclability accomplished using floating time experiments, it can be seen that after 160 k cycles, one has almost the same values found at 18h. Further discussions in the following sections based on the *operando* Raman findings will show a stretch/damage in the carbon network for voltages above 1.8V, which is in agreement with what was verified in the electrochemical studies.



**Figure 14.** Electrochemical data for the cyclability tests of the cell filled with the  $17 m \text{ NaClO}_4$  electrolyte. (a) Capacitance, (b) Energy and Power retention as a function of the charge-discharge cycles.

From the EIS data, the complex capacitance analysis  $(e.g., C(\omega) = C'(\omega) - jC''(\omega))$ permits the study of dissipative effects in SCs as a function of the applied frequency [151–154]. It is well-known that only the real part of the capacitance  $(C'(\omega))$  is usable in practical applications, while the imaginary part of the capacitance  $(C''(\omega))$  is responsible for energy dissipation. In this context, we interpret the complex capacitance data to complement our study involving the ESW values. **Figure 15(a)** shows the real capacitance part as a function of the frequency for the 1, 5, 10, and 17 *m* solutions. First, it is noted that the real part of the capacitance increases to a maximum as the frequency decreased. Taking into account the intrinsic properties of the electrode/electrolyte interface, this behavior is typical of EDLCs. Similar behavior was observed in the GCD study (**Figure 13(d**)), confirming an internal consistency between the different experimental approaches.

The imaginary part of the capacitance showed in **Figure 15(b)** is related to the irreversible energy dissipation in SCs. Knowing the characteristic frequency ( $f_0$ ) corresponding to a maximum C'' value, which occurred between 0.1 and 1 Hz in the present study, it is possible to determine the time constant ( $\tau_0 = 1/f_0$ ) for the device. This peak frequency defines the so-called *dielectric relaxation time*, normally used to study the ionic transport through the electrode microstructure [151,155]. The  $\tau_0$  value represents the minimum time required to discharge all the stored energy with at least 50% efficiency [155]. As seen in **Figure 15(b**), the lowest value of 1.2 s, which indicates an excellent energy delivery, is observed for the 10 m NaClO<sub>4</sub> solution. Also, the 5 m and 17 m electrolytes yielded very close dielectric relation times of 3.0 and 3.1 s, respectively. In the case of the 1 m solution, the device exhibited the highest

value of 7.7 s. This finding is another indication that high-concentrated electrolytes have a positive effect on the overall behavior of SCs, taking the precaution that the ESW is correctly established.

As seen, it was not verified a correlation between capacitance and concentration values. This behavior comes from the fact that ionic-water-based solutions exhibit non-linear physicochemical properties due to the short-range coulombic interactions [137]. Some noteworthy examples are Bjerrum's theory of the Ionic Association phenomenon and Fuoss and Kraus's theory for Triple Ions and Quadrupoles' formation. The complexity of the concentrated aqueous-based electrolytes was thoroughly discussed by Harned and Owen [133] and Robinson and Stokes [156].



**Figure 15.** (a-b) The dependency of the real (C') and imaginary (C'') parts of the capacitance as a function of the frequency. Capacitance data contrasting the cyclability tests for 1 m (c-d) and 17 m (e-f) NaClO<sub>4</sub> solutions.

It was contrasted in **Figure 15(c-d)** and **Figure 15(e-f)** the experimental findings obtained for the 1 m and 17 m solutions, respectively, as a function of the floating time experiment to get a better view of the effectiveness of the WiSE system with a ESW of 1.8 V

(17 *m*). Here, as in **Figure 13**, the EIS plots were obtained during the cyclability tests. As shown in **Figure 15(f)**, the 17 *m* WiSE-based device has excellent cycling stability demonstrated by the negligible changes after 18 h of floating time at 1.8 V. These findings confirmed that the 17 *m* NaClO<sub>4</sub> aqueous electrolyte exhibits the highest ESW (1.8 V) and ensured excellent cyclability conditions.

As can be seen, the relaxation time constant ( $\tau$ ) determined using the EIS technique does not correlate with the electrolyte concentration. In general, the theoretical analysis concerning the EDL structures in the presence of highly concentrated electrolytes is not straightforward. The theoretical expression for the *local dielectric constant* ( $\varepsilon(x)$ ) is not always possible (*e.g.*, the Booth's model). From a theoretical viewpoint, the electrochemical activity ( $\mu^{\rho}$ ) of the electrolyte species and the local electrical permittivity at the '*inner*' and '*outer*' Helmholtz compact layers are complex functions of the bulk concentration of the ionic species. It is also well-known from the Böckris-Devanathan-Müller EDL model that the oriented dipoles also affect the practical (measured) interface capacitance [137]. Theoretical models for the EDL capacitance using statistical mechanics were extensively discussed by Goodisman [131]. In any case, the EDL models are further complicated in the case of rough/porous electrodes. The advances regarding the EDL models for carbon-based electrodes used in SCs were recently discussed by Da Silva *et al.* [38].

## **3.3.2.** Operando Raman studies under constant voltage conditions using the single-step chronoamperometric method

A rational experiment to understand the carbon/WiSE interface can be performed using the *operando* Raman in conjunction with different electrochemical techniques. Carbon-based electrode materials, mainly the *activated carbons* (AC), are largely applied in SCs due to their intrinsic properties, such as high *specific surface area* (SSA) and good electrical conductivity. However, due to experimental difficulties found during the *operando* Raman studies using highly-porous electrode materials, it is used in the current work a 'model carbon electrode' based on graphite which has a well-defined Raman signal (fingerprint) that permits to investigate some fundamental events that occur at the interface under *static* and *dynamic* polarization conditions.

In light of the above considerations, the graphite electrode can permit to access simultaneously the (i) D-band shifts due to the adsorption/desorption of ionic species and (ii) the G-band split due to intercalation/insertion of ions into micropores. On the contrary, using

AC can be hard to accomplish this study with confidence since the D & G Raman bands are too broad to quantify the different shifts. However, it is worth mentioning that the experimental findings obtained using graphite electrodes cannot be extrapolated to other carbon materials (AC, CNTs, etc.) in a straightforward manner.

To better understanding and tracking changes on the electrode and electrolyte during the determination of ESW, we choose the WiSE system with the best performance (*e.g.*, 17 *m* solution) for the *operando* Raman spectroscopy analyses under constant cell voltage conditions (*e.g.*, SS-CA experiments) (see **Figure 16**). Accordingly, the *operando* Raman studies at the *open-circuit voltage* (OCV) and 0 to 4 V were accomplished to force the cell to fail. **Figure 16(a)** presents the deconvolution of Raman spectra using Lorentzian and Gaussian functions. At the OCV, the four prominent graphite bands were observed, namely D,  $E_{2G}$ ,  $E_{2G}$ ', and 2D, which originated from the intervalley and intravalley double-resonance processes (**Figure S2(a-c**) – Supporting Information). A comparison of the influence of the OCV(*i*) and 3 V(*ii*) on the Raman first-order signal evidenced the differences in intensities, band positions, and the appearance of new bands (Please see **Figure 16(b)**).

The results from the first and second-order events verified in the operando study accomplished at constant voltages are shown in Figure 16(c). As expected, the increasing of ESW up to the overpotential of 4.0 V causes water electrolysis, and consequently, the oxygen evolution at the anode. Moreover, the absence or strong water reduction in the electrolyte leads the sodium salt to precipitate. Thus, it affects the optical path, *i.e.*, reduces the laser power that reaches the WE, causing a low signal-to-noise ratio (SNR) of Raman bands. Figure 16(d) shows the Raman shifts ( $\Delta \omega$ ) for the D-, E<sub>2G</sub>-, E<sub>2G</sub>'and 2D-bands as a function of the applied voltage. The bars between the panels show the applied voltage (U) corresponding to each collected spectrum. First, it was detected an intensity reduction in the D-band expected due to an increase in the number of ions covering the electrode surface and mainly interacting with dangling bonds, *i.e.*, defects. It is important to notice that the formation of SBI happens when the electrode is in contact with a high-concentrated solution (e.g., 17 m of NaClO<sub>4</sub>) [147,157]. Second, the emergence of a new band for applied voltages greater than 1.8 V, which was ascribed to the  $E_{2G}$ ' mode occurring in the 1600–1618 cm<sup>-1</sup> interval, was verified. This Raman signal can be attributed to the insertion of the ionic species in the host electrode material, which induced changes in the boundary layer symmetry or electronic effects. As suggested in the literature [158], the E<sub>2G</sub>' mode in Raman spectra represents the graphene sheets containing intercalated ions. Previous studies involving 'normal' electrolytes revealed the intercalation of  $ClO_4^-$  species in the graphite structure [149,159,160]. The E<sub>2G</sub>' vibrational mode signal increases with voltage, indicating that more and more graphene sheets intercalate ions. Intercalating ions in aqueous media became pronounced after the SBI breaking down. The E<sub>2G</sub> vibration mode of the G-band shifted ~10.5 cm<sup>-1</sup>, which is also an indication of the *graphite intercalation compound* (GIC) formation [147,161–163].

By fitting the doublets present in the first-order Raman spectra representing the  $E_{2G}$  and  $E_{2G}$ ' modes, it was provided a quantitative analysis of the GIC stage dependence with the applied voltage. **Figure 16(e)** shows the  $E_{2G}/E_{2G}$ ' relative intensities while the inset evidences the GIC stage number calculated according to recent reports [164,165]. The GIC stage reduction from n = 10 to n = 3 indicates that when intercalation starts, each graphite layer is surrounded by other 7 to 9 graphite layers. The phenomenon is finished by covering one side with an intercalated layer. At the same time, on the other side, the phenomenon involves another graphite layer [158,164]. As expected, when applying higher voltages of *ca*. 1.8 V to induce stress in the graphite lattice, the SBI undergoes structural damages permitting penetration of the ionic species into the graphite layers. As a result, the GIC stage is decreased. As can be seen in **Figure S2(d & e)** (Supporting Information), the SBI *breakdown* is also noticeable by the increased stationary current verified during the applied voltage (*operando* Raman experiments), *i.e.*, ~1 nA cm<sup>-2</sup> (U < 1 V), ~20 nA cm<sup>-2</sup> (U = 1.8 V), and ~40 to 60 nA cm<sup>-2</sup> (U > 2 V). This current behavior indicating the SBI breakdown also characterizes the occurrence of watersplitting.

In the case of D-band, Raman shift is governed by the accumulation of the ionic species promoted by the polarization conditions. It is related to *Kohn anomaly* reduction in the graphite electrode during adsorption, *i.e.*, local electrical field formed by charge accumulation modified by electrode-defective phonon scattering. Blue-shifts for the D- and 2D-bands on the applied voltage confirm the distortions in graphite layers during an increase of ion adsorption at the interface and even more during an intercalation process. The literature suggests that the latter process occurs because of the electronic doping and the increased in-plane (biaxial) lattice strain accompanying the ionic insertion process [166–168]. Distortions in the graphite layers are also verified from the D/G relative intensities shown in **Figure 16(d**). Despite the intensity reduction of the D-band at higher voltages, the D/G-ratio increased to ~1, indicating the occurrence of graphite damage. In other words, the ionic intercalation caused defects on graphite structures, and that can be measured using the *operando* Raman spectroscopy.

As already reported [158,164], reversible ionic intercalation into graphite is not expected to occur at low-stage GICs and in aqueous electrolytes, as observed in the present study. However, there is a strong indication that an increase in the applied voltage breaks the SBI layer, causing the insertion/intercalation of more ionic species and reducing the GIC stage from 10 to 3, *i.e.*, the presence of distortions and damages in the graphite layers. Cell deactivation (device's complete failure) confirms the ionic intercalation and/or insertion is an irreversible process. At this point, one can relate the ionic intercalation and the different GIC stages with the best ESW of 1.8 V determined previously in the electrochemical studies.



**Figure 16.** Raman findings obtained for the graphite/electrolyte interface on different static polarization conditions from 0 to 4 V (one excursion direction only to cell failure). Electrolyte (WiSE): 17 m NaClO<sub>4</sub> solution. Experiments were carried out at constant voltages applied for 5 min, and a Raman acquisition time of 55 s with 1 accumulation was used throughout.

# **3.3.3.** Operando Raman studies under dynamic voltage conditions using cyclic voltammetry

To better understand what happens during the charge-discharge processes in WiSE systems with different concentrations and the appropriate ESW, further *operando* Raman studies were carried out under dynamic polarization conditions using the CV technique, *i.e.*, voltage here linearly changes over time. **Figure 17** presents the *operando* Raman spectra of graphite evidencing the first-order region for the different electrolytes ((**a**) 1, (**b**) 5, (**c**) 10, and (**d**) 17 *m* of NaClO<sub>4</sub>). On the right-hand side of the spectra, one can see a vertical bar indicating the applied voltage. Except for **Figure 17(a)**, which has a low ionic concentration and the electrolyte band did not appear, the Raman spectra were composed of the strong ClO<sub>4</sub><sup>-</sup> band at ~985 cm<sup>-1</sup>, followed by the D, G, and D' characteristic bands.

The main discussion presented here will be focused on D-band due to its considerable shift. On the contrary, no significant shifts were verified for the G-, D'-, and 2D-bands (Please see **Figure S3(a-c)** in the Supporting Information) in the absence of water-splitting. Additional experiments with different electrolyte concentrations, from 1 to 17 *m* NaClO<sub>4</sub>, in the absence of an applied external electric field and electrolyte, were both accomplished. The corresponding findings can be seen in **Figure S3(d)** (Please see the Supporting Information). For better visualization of the experimental results, **Figure 17(e-h)** shows data extracted from **Figure 17(a-d)** presented as a Raman shift ( $\Delta \omega$ ). All Raman spectra were deconvoluted using Lorentzian and Gaussian functions (Please see **Figure S3(e-g)** in the Supporting Information).



**Figure 17.** First-order Raman spectra of the graphite/electrolyte interface under dynamic polarization conditions using the CV technique. Electrolyte: (a) 1, (b) 5 or (c) 10, and (d) 17 *m* NaClO<sub>4</sub>. D-band shift position as a function of applied voltage: (e) 1, (f) 5, (g) 10, and (h) 17 *m* of NaClO<sub>4</sub>. Experiments were carried out at 1 mV s<sup>-1</sup>, and a Raman acquisition time of 55 s with 1 accumulation was used throughout.

Moreover, the Y-axis at the right shows the current response during *operando* Raman studies. There is a slight variation in current as a function of the electrolyte concentration. It is evident that despite the concentration that there was a pronounced D-band reversible blue shift. The D-band shifts observed for the 17 *m* and 1 *m* electrolytes were  $6 \pm 0.5$  cm<sup>-1</sup> and  $2 \pm 0.5$  cm<sup>-1</sup>, respectively. The shift ( $\Delta \omega$ ) shown in **Figure 17(e-h**) has a linear dependence related to electronic properties on the surface of the electrodes, which is known as the *Stark effect* [47–50,169] that affects the *Kohn's anomaly* [13,44]. This phenomenon occurs when a voltage is applied, causing a variation in the electrode Fermi level, thus reducing the electron-phonon interactions as previously discussed. As a result, the phonon vibration frequency increases; a tremendous ionic surface excess at the solution-side of the interface can enhance the Stark effect.

As previously reported by Inaba *et al.* [77], the ionic species from NaClO<sub>4</sub> solutions can go through intercalation or insertion processes when the electrode is subjected to a strong surface electric field. The ionic insertion between the most external (superficial) graphite layers causes structural defects and lattice stress, changing the phonon's vibration frequency. **Figure S3(h)** (Supporting Information) shows an experiment in the absence of an electrolyte to confirm that assertion. Therefore, the number of ionic intercalated species from the electrolyte causes the changes in the Raman spectra; the greater the concentration, the more significant the shift ( $\Delta \omega$ ).

### 3.4. Conclusion

This work reported a systematic study regarding the effect of WiSE concentration on the ESW of EDLCs. Through electrochemical studies based on EIS and SS-CA techniques, it was possible to define the best NaClO<sub>4</sub>–based WiSE concentration and ESW of 17 *m* and 1.8 V, respectively. The use of the impedance method (EIS) to verify the absence of undesired faradaic (parasitic) currents, based on the linear low-frequency response verified in the complex-plane plots (phase angle close to  $-90^{\circ}$ ), and verification of the exponential current transients with negligible background currents during the single-step chronoamperometric (SS-CA) experiments, are the main points deserving attention in this work. The cyclability tests under high-stress conditions using the floating time approach proved the good cycling characteristics of the graphite/WiSE electrochemical system. Long-term cyclability tests using GCD also confirmed that. Furthermore, *operando* Raman studies under dynamic (CV) and static (SS-CA) voltage conditions were of paramount importance to study the basic phenomenon behind the charge-storage process. Moreover, this work presents the first Raman *operando* observation regarding the influence of highly concentrated NaClO<sub>4</sub> electrolytes onto graphite resulting in shifts of the D-band and the SBI breakdown for voltages higher than 2 V. Up to voltages of 1.8 V, the SBI formation appears to be stable and reversible, but there are indications that the SBI layer is disrupted apart at 2 V; the  $E_{2G}$ '-band evidenced that ClO<sub>4</sub><sup>-</sup> intercalation into graphite layers brings water to attain the local neutrality in the active sites permitting the occurrence of water-splitting. For very high voltages of 2–4 V, the GIC formation increases, suggesting that high polarization conditions accelerate the intercalation process. In general, the current efforts bring new insights about the WiSE/graphite interface, presenting new experimental tools and a basic theoretical framework to aid the identification of the ESW for EDLCs.

# Chapter 4 Discussions and conclusions

This work presents a comprehensive exploration of double-layer caapcitors, *i.e.*, Supercapacitors (SCs), through the application of operando Raman spectroscopy, shedding light on the processes occurring during device operation. The first part of the study, specifically Chapter 2, focuses on fundamental investigations involving molecular dynamics simulations and operando Raman studies of polycrystalline graphite electrodes in different electrolytes. A comparison between highly oriented pyrolytic graphite (HOPG) with a smooth surface morphology and graphite with a rough surface morphology reveals higher capacitance values for the latter, suggesting that factors beyond surface roughness contribute to enhanced capacitance. The Raman operando analysis establishes a correlation between reversible D-band shifts, blue-shift of the 2D-band, and the accumulation/depletion of different cations at the graphite/electrolyte interface. The reversible reduction of Kohn's anomaly blueshift in the LO phonon branch at the K point further supports these observations. Molecular dynamics simulations provide insights into the theoretical calculation of the D-band deviation relative to the surface ionic charge, suggesting that the graphite-charge interaction with solvated cations, both at the electrode surface (surface excess) and from absorbed solvated cations, predominantly governs the observed D-band shifts. In Chapter 2, we validated this powerful Raman tool by applying it to various electrolytes and different laser wavelengths. We successfully correlated spectral analysis with electrochemistry, validating everything through computational simulation. Through this well-aligned approach, this Chapter elucidated the phenomenon of the D-band shift in carbon spectra, a commonly observed phenomenon in numerous literature works.

With this powerful tool, we decided to apply it to a more complex system, aiming to validate and create new perspectives and analysis tools for the hot scientific topic known as *Water in Salt Electrolyte* (WiSE). In the second part of the study, specifically **Chapter 3**, Raman spectroscopy under operando conditions is employed to investigate electrochemical systems utilizing superconcentrated electrolytes. These electrolytes enable SCs to operate within larger WVW. By replacing water dipoles with ions through high salt concentrations, a

"barrier" forms at the electrode/electrolyte interface, reducing the internal potential experienced by the interface. This increase in the SC's work potential significantly enhances its energy density. A systematic study is conducted to explore the effect of WiSE concentration on the WVW of SCs, with accurate electrochemical studies utilizing various techniques such as CV, EIS, and SS-CA. The optimal WVW and WiSE concentration are determined to be 1.8 V and 17 m, respectively. EIS and SS-CA studies confirm the absence of undesired faradaic currents, as indicated by angles close to -90° at low frequencies in the complex plane and currents approaching zero after the transient period in chronoamperometry studies. These findings are further supported by cycling tests conducted at 1.8 V and 17 m using the floating time approach and GCD techniques.

Raman spectroscopy under operando conditions is employed to corroborate the electrochemical findings, both under constant voltage conditions (SS-CA studies) and dynamic voltage conditions (CV studies). The results obtained in the second part of the study reveal, for the first time, the influence of highly concentrated NaClO<sub>4</sub> electrolytes on graphite, leading to D-band shifts and the breakdown of the SBI for voltages exceeding 2 V. The stability and reversibility of the SBI are observed for voltages up to 1.8 V, while indications of SBI rupture become apparent at higher voltages. The formation of the  $E_{2G}$ -band beyond 2 V suggests the interaction of  $ClO_4^-$  ions with graphite layers, facilitating water reaching local neutrality at the active sites and allowing water-splitting to occur. his phenomenon is further substantiated by the observation of the Raman spectral segment typical of  $ClO_4^-$  ions at higher voltages, providing additional evidence for this interaction. Increasing the voltage from 2 to 4 V significantly enhances the growth of graphite GICs, highlighting the accelerated intercalation process under high voltage conditions and consequent water-splitting.

In conclusion, this study introduces new tools for the investigation of SC devices. The application of Raman spectroscopy under operando conditions enables a deeper understanding of the desorption and adsorption processes of electrochemical species within SCs, surpassing the limitations of solely considering electrostatic processes. Furthermore, Raman operando analysis serves as a valuable tool for elucidating the processes occurring at the interface of superconcentrated electrolytes, as demonstrated in **Chapter 3**, which provides insights into GIC formation and indicates voltage windows that may not be suitable for SC operation. Together, **Chapters 2** and **3** constitute groundbreaking advancements in the field, as they not only uncover novel aspects of SC operation but also introduce innovative techniques that hold

immense promise for future discoveries. In particular, the application of operando Raman spectroscopy, featured prominently in these chapters, emerges as a pioneering tool that can revolutionize our understanding of SCs.

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## Appendix

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