

UNIVERSIDADE ESTADUAL DE CAMPINAS Faculdade de Engenharia Elétrica e de Computação

Lenon Henrique da Costa

Development of carbon and metal oxide based pseudocapacitor device and analysis operando using Raman spectroscopy

Desenvolvimento de dispositivo pseudocapacitor a base de carbono e óxidos metálicos e análises em operação utilizando espectroscopia Raman

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Thesis presented to the School of Electrical and Computer Engineering of the University of Campinas in partial fulfillment of the requirements for the degree of Doctor in Electrical Engineering, in the area of Electrical Energy.

Tese apresentada à Faculdade de Engenharia Elétrica e de Computação da Universidade Estadual de Campinas como parte dos requisitos exigidos a obtenção do título de Doutor em Engenharia Elétrica, na área de Energia Elétrica.

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Este trabalho corresponde à versão final da tese defendida pelo aluno Lenon Henrique da Costa, orientada pelo Prof. Dr. Hudson Zanin.

> Campinas 2022

Ficha catalográfica Universidade Estadual de Campinas Biblioteca da Área de Engenharia e Arquitetura Rose Meire da Silva - CRB 8/5974

Costa, Lenon Henrique da, 1992-Development of carbon and metal oxide based pseudocapacitor device and analysis operando using Raman spectroscopy / Lenon Henrique da Costa. – Campinas, SP : [s.n.], 2022. Orientador: Hudson Giovani Zanin.

Tese (doutorado) – Universidade Estadual de Campinas, Faculdade de Engenharia Elétrica e de Computação.

1. Supercapacitores. 2. Nióbio. 3. Espectroscopia Raman. I. Zanin, Hudson Giovani, 1983-. II. Universidade Estadual de Campinas. Faculdade de Engenharia Elétrica e de Computação. III. Título.

Informações para Biblioteca Digital

Título em outro idioma: Desenvolvimento de dispositivo pseudocapacitor a base de carbono e óxidos metálicos e análises em operação utilizando espectroscopia Raman Palavras-chave em inglês: **Supercapacitors** Niobium Raman spectroscopy Área de concentração: Energia Elétrica Titulação: Doutor em Engenharia Elétrica Banca examinadora: Hudson Giovani Zanin [Orientador] Aline Maria Pascon Cesar José Bonjuani Pagan **Gustavo Doubek** Tiago Almeida Silva Data de defesa: 15-03-2022 Programa de Pós-Graduação: Engenharia Elétrica

Identificação e informações acadêmicas do(a) aluno(a)

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Comissão Julgadora - Tese de Doutorado

Candidato: Lenon Henrique da Costa, RA: 192682

Data da defesa: 15/03/2022

Título da Tese: Development of carbon and metal oxide based pseudocapacitor device and analysis operando using Raman spectroscopy

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I dedicate this work to my parents, Edinéa and Carlos, for offering me the best education I could have.

ACKNOWLEDGMENTS

This except will be written in Portuguese.

Agradeço ao Prof. Dr. Hudson Giovani Zanin pela oportunidade, paciência e apoio ao longo dos últimos cinco anos. Ao Prof. Dr. Leonardo Moraes da Silva pelo suporte em relação a eletroquímica, incentivo e inspiração como profissional em relação ao trato com as pessoas e dedicação. Ao Prof. Dr. Tiago Almeida Silva, pela colaboração e apoio essencial na reta final do doutorado.

Aos meus amigos Danilo e Paula (ordem alfabética!) pelo entusiasmo, atenção, cuidado e apoio até aqui. A Giovana U. Valent, pelo carinho. A Prof.a Dr.a Cristiane F. Freitas por me apresentar à Unicamp, e ao Cléber e a Flávia pela as inúmeras caronas entre Campinas e Poços de Caldas.

A todas e todos os professores que tive até aqui, especialmente: Prof.a Luiza e Prof. Fernando, meus primeiros professores de matemática e física respectivamente, e Prof. Dr. Luiz F. Delboni e Prof. Dr. Francislei J. da Silva. E ao Prof. Dr. Marco A. R. Mello, pelo seu compromisso em treinar jovens cientistas, o qual reverberou em meu trabalho e foi essencial na minha jornada (nos vemos em *Valinor*).

Aos meus amigos & colegas de laboratório, especialmente: Dr. Alfredo Peterlevitz, Carla Real, Dr. Davi Soares, Erick Santos, Dr. Helder Ceragioli, João Pedro Santos, Manuel Pinzón, Prof. Dr. Mauro Amorin, Otávio Vilas Boas, Rafael Vicentini, Raissa Venâncio, Renato Beraldo, Thayane Alves e Willian Nunes.

O presente trabalho foi realizado com apoio do processo nº 2017/19222-4, da Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP).

ABSTRACT

The development of energy storage devices is vital nowadays. There is an increasing demand for products and energy generation sources using supercapacitors and batteries, such as electric vehicles and wind power. Supercapacitors suffer from low energy density, but they provide high power density and can be charged and discharged hundreds of thousands of times. In this sense, this work aims at developing a device that combines non-faradaic double-layer reactions (typical of supercapacitors) and faradaic pseudocapacitive reactions (typical of batteries). Flexible and self-supporting multiwalled carbon nanotubes (MWCNTs) electrodes were produced and functionalized by oxygen-plasma (OPF) treatment. The as-prepared and OPF treated electrodes were studied by electrochemical methods in a symmetric configuration using a neutral aqueous electrolyte. The MWCNTs were also used as a scaffold for flexible and selfsupported activated carbon (AC) electrodes, a capacitive porous material with a high surface area, and orthorhombic niobium pentoxide (T-Nb₂O₅), a pseudocapacitive material due to the rapid intercalation of Li⁺ ions. These two types of electrodes were analyzed by electrochemical methods in asymmetric configuration and using an organic electrolyte. These devices' development also depends on advances in understanding the chemical phenomena at the electrodes' surface and the electrode/electrolyte interface. For this reason, in situ and operando Raman spectroscopy studies were performed, focusing on the T-Nb₂O₅ pseudocapacitance reactions (negative electrode). Results of the present study confirm that high surface area carbon electrodes can improve the electrical characteristics of supercapacitors. Especially MWCNTs, which provide high power densities and present excellent electrical properties, have been proved a great scaffold. That is why they were used together with AC and T-Nb₂O₅. Although a higher increase in energy storage was initially expected with the plasma-induced surface changes, MWCNTs per se suffer from low energy density because their inner multiples walls are not electrically active. However, a theoretical model was proposed to understand the distributed capacitance behavior and the influence of the electrolyte resistance inside the different pores on the charge-storage process. Time constants involved in each process need to be considered in the interaction between faradaic and non-faradaic reactions, i.e., between capacity (Coulomb) and capacitance (Farad). The distributed capacitance applied to pseudocapacitance devices and electrodes has been proved an excellent way to assess and enable this complex interaction. The T-Nb₂O₅ allows a fast faradaic reaction of lithium-ion diffusion throughout the bulk of the active material. The operando Raman analysis was crucial for clarifying the electrochemical mechanisms of the material and its surface, as well as the Li⁺ intercalation potentials at asymmetric configuration. Typical battery electrodes and essentially capacitive electrodes were successfully combined. The T-Nb₂O₅ intercalation pseudocapacitance reaction was fast enough to enable a high-power energy storage device. It stores 45% and ~2.5 times more energy than an AC based supercapacitor, considering charge-discharge times between 5 seconds and 2 minutes, respectively, in the same conditions and with similar power capabilities.

Keywords: energy storage in supercapacitors; pseudocapacitance; *operando* Raman spectroscopy; niobium pentoxide; carbon and metal oxide materials.

RESUMO

O desenvolvimento de dispositivos armazenadores de energia tem grande importância no cenário mundial atual, que cada vez mais demanda por produtos e por fontes de geração de energia que utilizam supercapacitores e baterias, tais como os carros elétricos e a energia eólica. Supercapacitores sofrem com baixa densidade de energia, porém são dispositivos que disponibilizam alta densidade potência e que podem ser carregados e descarregados centenas de milhares de vezes. Nesse sentido, o objetivo desse trabalho foi desenvolver um dispositivo que combinasse processos não-faradaicos de dupla camada elétrica (típico de supercapacitores) e processos pseudocapacitivos faradaicos (típicos de baterias). Eletrodos flexíveis e autossuportados de nanotubos de carbono de paredes múltiplas (NTCPM) foram produzidos e funcionalizados por plasma de oxigênio. Esses eletrodos com e sem funcionalização foram estudados por métodos eletroquímicos em configuração simétrica e utilizando eletrólito aquoso neutro. NTCPMs também foram utilizados como estrutura suporte de eletrodos flexíveis e autossuportados de carvão ativado (CA), material capacitivo poroso de alta área superficial, e de pentóxido de nióbio ortorrômbico (T-Nb₂O₅), material pseudocapacitivo devido a rápida intercalação de íons Li⁺. Ambos os eletrodos foram estudados por métodos eletroquímicos em configuração assimétrica e utilizando eletrólito orgânico. O desenvolvimento desses dispositivos também depende de avanços na compreensão dos fenômenos químicos da superfície dos eletrodos e da interface entre eletrodo/eletrólito. Por esse motivo, análises de espectroscopia Raman in situ e em operação foram feitas com foco no processo de pseudocapacitância do eletrodo de T-Nb₂O₅ (eletrodo negativo). Os resultados do presente trabalho confirmam que eletrodos de carbono de alta superficial podem melhorar as características elétricas de supercapacitores. Especialmente os NTCPMs, os quais propiciam altas densidades de potência e têm excelentes propriedades eléctricas, demostraram ser um ótimo material de suporte para outros materiais, e justamente por isso eles foram utilizados em conjunto com CA e T-Nb₂O₅. Embora fosse esperado um aumento maior no armazenamento de energia por meio da funcionalização, também foi notado que NTCPMs per se sofrem de baixa densidade de energia devido as suas paredes múltiplas internas não serem eletricamente ativas. Contudo, o estudo destes dispositivos permitiu propor um modelo teórico para representar o comportamento da capacitância distribuída e da influência da resistência ôhmica do eletrólito no interior dos poros do material no processo de armazenamento da carga. A interação entre reações faradaicas e não-faradaicas, i.e., entre capacidade (Coulomb) e capacitância (Farad), precisa considerar as constantes de tempo envolvidas em cada processo. A *capacitância distribuída* aplicada a dispositivos e eletrodos pseudocapacitivos se mostrou um ótimo meio de avaliar e viabilizar essa interação complexa. O T-Nb₂O₅ permite uma rápida reação faradaica de difusão de íons de lítio através da estrutura do material ativo. Neste sentido, a análise Raman *in situ* e em operação foi crucial para esclarecer os mecanismos eletroquímicos do material e da sua superfície, assim como as voltagens de intercalação do Li⁺ no dispositivo assimétrico. Foi possível combinar elétrodos típicos de bateria e eletrodos essencialmente capacitivos. A reação pseudocapacitiva de intercalação do T-Nb₂O₅ foi suficientemente rápida para viabilizar um armazenador de energia de alta potência que armazena 45% e ~2,5 vezes mais energia que um supercapacitor com eletrodos de CA, considerando tempos de carga e descarga entre 5 segundos e 2 minutos, respectivamente, nas mesmas condições e com capacidades de potência semelhantes.

Palavras-chave: energia armazenada em supercapacitores; pseudocapacitância; espectroscopia Raman *in situ* e em operação; pentóxido de nióbio; materiais de carbono e óxidos metálicos.

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Chapter 1

1. General introduction

The development of the capacitor technology began in 1745 when Ewald Georg von Kleist and Pieter van Musschenbroek concurrently built the earliest capacitors, called *condensers* at the time [1,2]. This device, a *Leyden jar*, as it is known even today, can store electric charges (and consequently energy). The bigger the jar, i.e., a glass dielectric, the larger the area to store charges and then the capacitance. The unit of capacitance, after all, was *jar* until 1872, later changed to Farad (F), in memory of Michael Faraday [1].

Howard I. Becker, in 1954, proposed the first double-layer device (U.S. Patent 2800616A), a never commercialized *Low voltage electrolytic capacitor*, later improved by Robert A. Rightmire (1962) and Donald L. Boos (1970) [3]. The concept of the double-layer itself arose a century earlier, in 1853, in a work of H. L. F. von Helmholtz on *the distribution of electric currents in volume conductors* [4–6], applied in electrochemistry based on the classical parallel-plate capacitor model [7]. Regarding pseudocapacitors, Trasatti and Bazzanca in 1971 [8] related the *capacitor-like* behavior of ruthenium dioxide films, a surface-redox pseudocapacitance behavior, accordingly to Conway *et al.* [9] fundamental works.

Comprising almost three centuries of technological evolution: the *Layden jar* has become the capacitor technology traditionally used in electronic devices and transmission and distribution systems to provide reactive power compensation, while the first double-layer capacitors have become today's supercapacitors used to suppress other devices' weaknesses, like batteries and fuel cells low power density.

1.1 The energy storage mechanism for supercapacitors

Supercapacitors are mostly known as electric double-layer capacitors (EDLCs) and pseudocapacitors (PCs).

EDLCs store charges electrostatically by reversibly adsorbing ions from the electrolyte onto electrochemically stable materials of high surface area carbon electrodes, such as activated carbon (AC). Their charging process, or electrical charge separation, occurs due to the polarization of the electrode & electrolyte interface, producing what Helmholtz described as a double-layer [6].

Regarding the Helmholtz model based on the classical parallel-plate capacitor model, Gouy and Chapman later suggested the presence of a diffuse layer in the electrolyte due to the ions accumulation near the electrode surface, and Stern (1924) and Grahame (1947) developed the model usually referred to Stern's model [7]. Stern's model considers the specifically adsorbed ionic species and combines the Helmholtz and Gouy and Chapman models in series [7]. Bockris, Devanathan, and Müller (BDM) then refined these views by considering the relative local dielectric constant of the electrolyte, treated as solvent's dipole molecules [7,10].



Figure 1: (a) Helmholtz, (b) the so-called Stern model, and (c) a simplified representation of the BDM contribution regarding the relative local dielectric constant of the electrolyte and the solvent's dipole molecules. The inner Helmholtz plane (IHP) refers to the closest (adsorbed) ions and Outer HP to those furthest away (non-adsorbed). OHP is also the place where the diffuse layer starts; *d* is the distance of the double layer. Adapted from [7,9].

Starting from the classical parallel-plate capacitor expression:

$$C = \frac{(\varepsilon_r \varepsilon_0) A}{d},\tag{1}$$

for an ideal flat supercapacitor, ε_r is the relative local dielectric constant of the electrolyte (dimensionless); ε_0 is the permittivity constant of vacuum (pF·m⁻¹); *d* is the effective thickness of the double layer in meters (m); and *A* is the surface area of the interface, in square meters (m²). One then has an approximation that does not consider the pore geometry.

The Helmholtz compact layer is predominant in a supercapacitor using concentrated electrolytes (e.g., 1 mol). In this case, the diffuse layer is negligible [7]. Nevertheless, the dielectric constant of the electrolyte is *relative*, so in the absence of specific adsorption ions and considering a plane surface, accordingly to the BDM model, the capacitance C^1 is [7,11]:

$$\frac{1}{C} = \frac{4\pi 2r_w}{\varepsilon_L} + \frac{4\pi\sqrt{3}r_w}{\varepsilon_H} + \frac{4\pi r_i}{\varepsilon_H},$$
(2)

where $2r_W$ is the thickness of the primary water layer, and r_i is the radius of the non-hydrated ion at the OHP [7]. The lower relative permittivity ε_L is associated with the oriented dipoles of the primary layer (please see **Figure 1 (c)**), for water $\varepsilon_L = 6$ while ε_H has values between 32 and ~78 [7,12]. Thus, the oriented dipoles closest to the electrode surface ruled the capacitance regarding the relative permittivity.

Therefore, assuming that ions are point charges, as in Equation (1), the energy stored during the reversibly adsorbing ions process is equal (i.e., disregarding losses) to the energy required (i.e., work) to gather these charges. Considering n point charges and an initially uncharged region, the interaction between the electric field generated by each charge and the work (W_E) required for its accumulation in this region of space is:

$$W_E = \frac{1}{2} \sum_{k=1}^{n} Q_k V_k , \qquad (3)$$

where: Q is point charge (C), V is electric potential (J C⁻¹).

For a continuous distribution of charges, we consider the integral of the volume density of charges (ρ_v) in the region:

$$W_E = \frac{1}{2} \int_{v} \rho_v V dv , \qquad (4)$$

since the divergence of the electric flux density $(\nabla \cdot \mathbf{D})$ is equal to the volume density of charges (Gauss's Law), we can rewrite Equation 4 from vector identities and apply the divergence theorem. Thus, for a large electrically charged surface, Equation 4 is expressed as follows [13]:

$$W_E = -\frac{1}{2} \int_{v} (\mathbf{D} \cdot \nabla V) dv$$
 (5)

The electric field (E) equals to minus the electric potential gradient ($\mathbf{E} = -\nabla V$) and the electric flux density $\mathbf{D} = \varepsilon_0 \mathbf{E}$, rewritten in Equation 5, results in:

$$W_E = \frac{1}{2} \int_{v} (\varepsilon_0 \cdot E^2) dv$$
 (6)

The symmetry between the charge accumulation in the double electric layer of a supercapacitor electrode and the electric charge accumulation of a parallel plate capacitor for an ideal case (no scattering of the electric field at the plates or electrodes edge) allows us to use the electric field deduction for an infinite plate for both cases:

$$E = \frac{-Q}{\varepsilon_r \varepsilon_0 A},\tag{7}$$

therefore, using the definition of capacitance C = Q/V, Equations 6 & 7 demonstrate that the energy in a supercapacitor is:

$$W_E = \frac{1}{2} \int_{v} \left(\frac{\varepsilon_r \varepsilon_0 \cdot Q^2}{(\varepsilon_r \varepsilon_0)^2 A^2} \right) dv = \frac{\varepsilon_r \varepsilon_0 Q^2 A d}{2A^2} = \frac{Q^2}{2} \left(\frac{d}{\varepsilon_r \varepsilon_0 A} \right) = \frac{Q^2}{2C}$$
(8)

$$W_{supercapacitor} = \frac{Q^2}{2C} = \frac{1}{2}QV = \frac{1}{2}CV^2 \tag{9}$$

The energy of a capacitive energy storage device can also be deduced from its discharge curve at a constant change rate, i.e., employing a constant current (in ampere, A). In this case, the energy in the device is numerically equal to the discharge curve area (V = J/C, Joule per coulomb) multiplied by the constant current (A = C/s, coulomb per second).



Figure 2: Energy stored in a capacitive device.

It is crucial to notice that Equation 9 is only applied if the supercapacitor's Galvanostatic Discharge Curves (GCD) have a triangular shape. The triangular plot in **Figure 2** can define the behavior of a capacitive device, i.e., the potential variation as a function of time $(\Delta V/\Delta t)$ is constant. Similarly, a constant potential variation (constant scan rate (SR) (V s⁻¹)), performed using Cyclic Voltammetry (CV), will result in a constant charge and discharge current.

This definition is handy since some materials present fast surface redox reactions with current behavior at a constant scan rate (SR) (V s^{-1}) rectangular shaped in a cyclic voltammetry

plot, *like a capacitor*. Nevertheless, this shape may not result from electrostatic processes, as in the case of ruthenium oxide in an acidic aqueous medium [8,9]. **Figure 3 (a & b)** illustrate this observation. In this sense, the prefix pseudo is used, etymologically from Greek *pseudēs*, meaning false, in appearance only, resembling. That is, a pseudocapacitor is similar to a capacitor (fast charge transfer) in appearance only (rectangular voltammetry), but it is not a capacitor (it does not store energy electrostatically).

Pseudocapacitance is also observed in specific potential windows with organic electrolytes. In a potential window wider than 1V, crystalline metal oxide structures with ample interplanar space allow ions to intercalate [7,9]. In this reaction, the material's peak current varies linearly with the potential variation, characteristic of non-diffusion-limited materials such as supercapacitors. However, the current of a supercapacitor is constant concerning the potential variation in regions not affected by the solution. Thus, the voltammetry in an intercalation pseudocapacitance electrode is not rectangular, but it is still similar to a capacitor with anomalous diffusion [7].



Figure 3: Pseudocapacitance behaviors. Adapted from [7].

These EDLCs and PCs devices and other electric energy suppliers such as batteries and electrostatic capacitors can be represented according to the specific power (W kg⁻¹) and specific energy (Wh kg⁻¹) they present, commonly in a so-called Ragone graph [14]. In a Ragone plot, the supercapacitor energy is at least six times smaller than a lead-acid battery, reaching ~5 Wh kg⁻¹ on 2.7V commercial devices. This gravimetric capacitance (C) can be determined as follows [7,9]:

$$C = \frac{I}{m\left(\frac{dV}{dt}\right)} \tag{10}$$

where: *I* is the galvanostatic current in ampere (A); dV/dt is the voltage variation as a function of the time of the GCD curve in volts per second (V-s⁻¹); *m* is the mass of active electrode material in grams (g); and *C* is gravimetric capacitance in farads per gram (F g⁻¹).

The energy (E) and average power (P) densities can be expressed generically through Equations 11 & 12, respectively:

$$E = \frac{C(\Delta V)^2}{2} \times \frac{10^3}{3600}$$
(11)

$$P = \frac{E}{\Delta t} \times 3600 \tag{12}$$

where: Δt is the galvanostatic discharge time interval in seconds (s); *C* is the gravimetric capacitance in farads per gram (F g⁻¹); ΔV is the voltage variation of the galvanostatic discharge curve in volts (V); *E* is the energy density in watt-hours per kilogram (Wh Kg⁻¹); *P* is the power density in watt per kilogram (W Kg⁻¹).

An expression specific to supercapacitors that do not consider the ohmic loss of the pores uses the concept of maximum power transfer, as follows [15]:

$$P_{\max} = \frac{\Delta V^2}{4R_s},\tag{13}$$

where R_s is the equivalent series resistance (Ω g) [16], ΔV is the voltage variation of the GCD curve in volts (V), and *P* is the power density in watt per kilogram (W Kg⁻¹).

One can use the relationship between *E* and P_{max} (Equations 11 & 13) to obtain the Ragone plot data following the expression [15]:

$$E_{L} = \frac{E_{\max}}{2} \left(1 + \sqrt{1 - \frac{P_{L}}{P_{\max}}} \right), \qquad (14)$$

where E_L and E_{max} are the dissipated energy in the load and the maximum energy, and P_L and P_{max} represent the load power and the maximum power transfer, respectively. Equation 14 is then solved using a numerical solution to obtain P_L and E_L .

It is important to remember that the active electrode material mass usually used in supercapacitor research does not consider the electrolyte, separator, case, and connections masses. Furthermore, it needs to follow good practice criteria, such as electrode masses on the mg (milligram) scale, to report the electrode and device's capacitance and energy [17–19].

1.2 Questions and general hypotheses

The current world scenario deals with several demands related to sustainability, which implies using renewable energy sources and developing solutions that enable the proper use of energy, *i.e.*, with final clean sustainable energy application.

At least 1/3 of current electricity generation is based in coal power plants [20]. Considering primary energy consumption by fuel, oil and coal account for half the planet's energy [21]. In this context, one might ask: How can we start? How many pieces make up this big puzzle?

Several of these puzzle pieces are connected to how we intend to store electrical energy. Batteries and supercapacitors are suitable devices for storing and providing electrical energy and power. Batteries present high energy density and provide it continuously and prolongedly, and supercapacitors are high-power systems that can perform thousands of fast charge and discharge cycles.

Supercapacitors are power systems that suffer from moderate energy, so the working question of this thesis is: *how to increase the stored energy in supercapacitor devices while maintaining their high cyclability and high-power density characteristics?*

Currently, the improvements in supercapacitors and batteries do not depend only on new materials but also on clarifying the electrochemical mechanisms of the surface, the solid-state (bulk) and the interfacial region of the electrodes. Within this perspective, several studies have been performed on the concept of operation dynamics (*in situ* and *operando*) [9-29]. One of the techniques used for this purpose is Raman spectroscopy, referred to as *operando* Raman analysis. Pseudocapacitive electrodes using asymmetric oxides and electrochemical capacitors can be better understood in this context.

Regarding the energy storage mechanism of supercapacitors, the present work uses Raman spectroscopy and electrochemical studies to investigate the following hypotheses: (i) different carbonaceous materials (micro and nanostructured) of high surface area, whether or not synthesized directly on the current collector, can improve the electrical characteristics of aqueous supercapacitors?, (ii) how the oxygen plasma functionalization process of these materials?; (iii) the junction of a battery-type electrode and an essentially supercapacitive (non-Faradaic) electrode are possible? Is Faradaic reaction fast enough?

This thesis structure follows an alternative format comprising two academic works (Chapters 2 & 3) and presents a study of our progress in developing better supercapacitors.

Chapter 2 investigates, through electrochemical methods, the energy enhancement of a supercapacitor in an aqueous medium, which ensures low toxicity and drastically decreases the production cost (no dry rooms or glove boxes are necessary). Self-supporting multi-layered carbon nanotubes (MWCNTs), knowns as MWCNTs buckypaper, were employed as the electrode. The carbon electrodes are excellent conductors, chemically active and stable in different electrolytes. In this approach, they were functionalized by oxygen plasma at different times. The oxygen plasma etching attached functional groups on its surface are directly related to the pseudocapacitance presented by these devices. In this chapter, we clarify the relative magnitude of pore electrolyte ohmic resistances ($R_{ESR} < R_{out} < R_{in}$) and highlight the power of concomitant uses of electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA) techniques. This chapter presents a theoretical analysis to understand the distributed capacitance behavior and the influence of electrolyte resistance inside the different pores on the charge-storage process.

In Chapter 3, activated carbon (AC) and orthorhombic niobium pentoxide (T-Nb₂O₅) were used as electrodes for two particular devices, one symmetric using AC as active material and another asymmetric using T-Nb₂O₅ and AC (see further discussion). The high surface area of activated carbon associated with the electrochemical stability of carbon makes it an indispensable material in supercapacitors. The T-Nb₂O₅ allows a fast Faradaic reaction of lithium-ion diffusion throughout the bulk of the active material. This reaction is faster than battery diffusion-limited Faradaic reactions but can be slow compared with a typical faradaic process in supercapacitors. In this context, we investigate the interaction between these Faradaic and non-Faradaic processes in a hybrid device.

Therefore, the present investigation resulted in two scientific papers:

Accessing the electrostatic and pseudocapacitive contributions for oxygen-plasma etched multiwalled carbon nanotubes buckypaper electrodes and the analysis of the distributed capacitance affected by the pore electrolyte resistance,

In situ Electrochemical and operando Raman spectroscopy investigation of T-Nb₂O₅ for pseudocapacitors,

and contributed significantly to the following five papers:

Direct growth of mesoporous Carbon on aluminum foil for supercapacitors devices R. Vicentini, **L.H. Costa**, W. Nunes, O. Vilas Boas, D.M. Soares, T.A. Alves, C. Real, C. Bueno, A.C. Peterlevitz, H. Zanin. J. Mater. Sci. Mater. Electron. 29 (2018) 10573–10582.

Highly stable nickel-aluminum alloy current collectors and highly defective multi-walled carbon nanotubes active material for neutral aqueous-based electrochemical capacitors R. Vicentini, W.G. Nunes, L.H. Costa, L.M. Da Silva, A. Pascon, P. Jackson, G. Doubek, H. Zanin.

J. Energy Storage. 23 (2019).

Surface and electrochemical properties of radially oriented multiwalled carbon nanotubes grown on stainless steel mesh W.G. Nunes, R. Vicentini, L.M. Da Silva, L.H. Costa, T. Tadeu, H. Zanin. J. Electrochem. Soc. 165 (2018).

Environmentally friendly functionalization of porous carbon electrodes for aqueous-based electrochemical capacitors

R. Vicentini, W.G. Nunes, L.H. Costa, A. Pascon, L.M. Da Silva, M. Baldan, H. Zanin. IEEE Trans. Nanotechnol. (2019).

In-situ electrochemical and operando Raman techniques to investigate the effect of porosity in different carbon electrodes in organic electrolyte supercapacitors R. Venâncio, R. Vicentini, L.H. Costa, R. Teófilo, L.M. Da Silva, H. Zanin. J. Energy Storage. 50 (2022) 104219.

Our research group has expertise in batteries and supercapacitors [7,15,16,43–82]. Finally, this project (FAPESP 2017/19222-4) has also contributed to starting the first *pouch cell* laboratory-scale prototype manufacturing of supercapacitors & batteries in Brazil [83].

Chapter 2

Accessing the electrostatic and pseudocapacitive contributions for oxygen-plasma etched multiwalled carbon nanotubes buckypaper electrodes and the analysis of the distributed capacitance affected by the pore electrolyte resistance

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Abstract

We discuss in this work the effect of oxygen plasma etching treatment on the overall charge-storage characteristics of multiwalled carbon nanotubes (MWCNTs) as electrode material for aqueous-based supercapacitors. The synthesized materials were ex-situ characterized by scanning electron microscopy, Raman, and X-ray photoelectron spectroscopies. Electrochemical experiments were accomplished using cyclic voltammetry, electrochemical impedance spectroscopy, single-step chronoamperometry, and galvanostatic charge-discharge. Different events accounting for the "porous electrode behavior" were discriminated in the time domain using the electrochemical techniques. A theoretical analysis was presented to understand the distributed capacitance behavior and the influence of the electrolyte resistance inside the different pores on the charge-storage process. The oxygen plasma etching treatment resulted in exfoliated MWCNTs with increased defective areas at the external interface, bringing them together by electrostatic forces and forming agglomerated structures of different sizes on the buckypaper top surface. In addition, the amount of surface oxygenated functional groups increased from ca. 2 to 30%. The overall charge-storage characteristics of the symmetric supercapacitor device increased by ca. 10% after the treatment. Not all oxygenated surface groups were electrochemically active. Therefore, the oxygen plasma etching treatment comprises a strategy to ameliorate the charge-storage properties of supercapacitors' carbon-based electrode materials. Specifically, the surface-modified MWCNTs allowed us to focus on a fundamental approach for studying the overall capacitance characteristics of nanostructured carbon-based electrodes. Thus, the charge-storage mechanism in the time domain and the individual contribution of the pseudocapacitance in the frequency

domain were studied to clarify the real electrochemical behavior exhibited by porous carbonbased electrode materials.

Keywords: oxygen plasma etching treatment; redox activity of oxygenated groups; multiwalled carbon nanotubes; energy storage in supercapacitors; analysis of the distributed capacitance.

1. Introduction

Supercapacitors (SC) are electrochemical devices with outstanding charge-storage and power characteristics that permit a rapid energy release in different circuit systems used in several technological applications [7,84,85]. That is possible owing to a particular charge-storage electrostatic mechanism based on the reversible adsorption-desorption of the ionic species at the porous electrode/electrolyte interface. Generally, supercapacitor (SC) properties such as specific power and energy can be improved by increasing the (*i*) *electrochemical active surface area*, (*ii*) the *pseudocapacitive contribution*, and (*iii*) the *working voltage window* (WVW) limited by the electrolyte stability [55]. As discussed in the literature, the main strategy for incorporating a pseudocapacitance in carbon-based materials to obtain well-behaved pseudocapacitors (PC) is based on the introduction of reversible solid-state surface redox reactions [7,19,84,85]. In principle, the surface of carbon-based electrode materials can be modified using different transition metal oxides (TMO) resulting in *surface* or *near-surface* reversible solid-state redox reactions mediated by the adsorption or intercalation, respectively, of the ionic species from the electrolyte [85–87].

A literature survey showed that redox surface processes in PCs characterized by fast solid-state redox reactions not governed by diffusive mass-transport of the ionic species permit very high capacitance retentions of *ca*. ~95% measured over more than a million charge-discharge cycles [7,54,59,88]. In these cases, the incorporated surface redox reactions are rapid electrochemical processes that behave similarly to a conventional electrostatic charge-storage process verified for electrical double-layer capacitors (EDLC), thus following the *electrostatic law* expressed by I = C(dU/dt), where I is the capacitive current, C is the experimental capacitance, and dU/dt = v is the voltage scan rate [7]. The latter parameter (v) is measured using the cyclic voltammetry (CV) and/or galvanostatic charge-discharge (GCD) techniques [19]. In this sense, we have that *well-behaved* PCs must also obey the same electrostatic law

verified for EDLCs, *i.e.*, the CV profiles must be practically featureless (*e.g.*, rectangular and symmetric), while the GCD curves must exhibit the characteristic triangular profile [7,89].

On the contrary, the incorporation of *slow faradaic processes* in carbon-based structures governed by the *solid-state diffusion* of the intercalating ionic species (*e.g.*, near-surface or bulky redox reactions) commonly results in a different electrochemical phenomenon characteristic of battery systems, *i.e.*, the so-called *battery-like behavior* [7,90–93].

Generally, the CV profiles obtained for battery-like systems are not featureless since they exhibit pronounced redox bands/peaks, *i.e.*, the analysis of CV data commonly reveals a linear dependency of the peak current with the square root of the scan rate, *i.e.*, $I = C(dU/dt)^{1/2}$. At the same time, the GCD curves are not linear during the discharge showing an almost constant voltage interval. Thus, we must consider the presence of a specific capacity (C^*/mA h g⁻¹) ascribed to batteries instead of the specific *pseudocapacitance* (C/F g⁻¹) when the CV and GCD data deviate from the expected EDLC behavior. It is worth mentioning from the applied viewpoint that a pseudocapacitance must be in accordance with the well-known SC intrinsic properties incurring in high-power performance. On the contrary, the presence of a *capacity* is of relevance to battery systems where the accumulation of high specific energies occurs at the expense of low power values [7]. In fact, from the practical viewpoint, supercapacitors and batteries are complementary devices used in different technological applications. Unfortunately, we can find in several literature reports absurd (or false) specific pseudocapacitance values (e.g., 1000 to 2500 F g^{-1}) due to the incorrect analysis or inappropriate interpretation of the capacity data [94–98]. This critical issue was recently discussed by some of the present authors [7].

In addition, the naive promises commonly found in some literature reports regarding the recipes for tailoring the properties of different electrode materials aiming an interconversion of the properties intrinsic to batteries and SCs into a single (hybrid) electrochemical system do not make sense from the practical viewpoint. It is impossible for a single electrochemical device to exhibit at the same time high specific energy and power values since the magnification of one parameter demands suppression of the other, *i.e.*, the time-scale of the physicochemical events inherent to SCs and batteries are linked to different phenomena occurring at the electrode/solution interface and in the bulky region of the electrode material, respectively [7].

Regarding the realistic improvement of the SC characteristics, we can found that the charge-storage characteristics exhibited by various carbon-based electrode materials used in EDLC can be improved using different chemical and physical treatments [99–101], where the

active surface area, which commonly deviates from the measured BET surface area, is increased and/or a pseudocapacitance is correctly introduced by incorporation of *redox-active oxygenated surface groups* [88].

A comprehensive discussion concerned with the influence of the surface functional groups present on carbon-based electrodes on the overall specific capacitance was previously presented by Deyang Qu [102]. As verified, the main electrochemically active structures are the quinoid, quinhydrone, phenolic, carboxyl, carbonyl, and lactone groups. In addition, Andreas and Conway [103] studied the capacitance of carbon cloth electrodes used in a supercapacitor for the purpose of evaluating the charge-storage process in the presence of different redoxactive surface groups as a function of the electrolyte *p*H. They verified a 30% loss in capacitance when the *p*H was changed from 0 to 11, which was ascribed to a reduction in redox activity of the quinone groups. At the same time, it was found for *p*H > 11 a capacitance increases of 20% due to the formation of different surface functionalities, *i.e.*, a pyrone derivative and another unknown species stable in strongly alkaline conditions.

The capacitive mechanism of oxygenated surface groups on carbon surfaces was also discussed by He *et al.* [101]. These authors proposed that in acidic solutions the quinone groups combine with the hydrated proton (H_3O^+) to transform the ketone group to the hydroxyl group, resulting in the movement of charge. The redox process was represented as follows [101]:

$$>C_xO+H_3O^++e^- \leftrightarrow >C_xOH(H_2O)$$
 (1)

where the symbol > describes the surface of the carbon material.

At the same time, these authors proposed for alkaline solutions the occurrence of the following redox process [101]:

$$> C_x O + [M(H_2O)_n]^+ + e^- \leftrightarrow > C_x OM(H_2O)_{n-y}$$
(2)

where *n* represents the number of water molecules coordinating the alkaline metal (M) from the electrolyte (*e.g.*, Li, K, Na, etc.), and *y* represents the number of water molecules lost by the hydrated cation during the reduction process. Despite these considerations, these authors did not present a theoretical analysis for neutral conditions commonly met in bench-scale SCs.

More recently, Vicentini *et al.* [88] proposed for carbon electrodes that in the presence of C=C groups a reversible electrostatic process can occur (*e.g.*, >C_xO + Li⁺ \leftrightarrow C_xO//Li⁺, where C_xO//Li⁺ represents the Li⁺ species adsorbed by a carbonyl or quinone-type site). In this sense, the electrostatic process results in an enhanced electrical double-layer capacitance due to the local changes in electronic charge density. In addition, the occurrence of a pseudocapacitance was predicted from the redox activity involving the oxygenated surface groups (*e.g.*, >C–OH \leftrightarrow >C=O + H⁺ + e⁻, –COOH \leftrightarrow COO + H⁺ + e⁻, >C=O + e⁻ \leftrightarrow >C–O⁻, and >C_xO + H⁺ + e⁻ \leftrightarrow C_xOH, where >C_xO represents a carbonyl- or quinone-type complex). Therefore, a combined electrostatic-faradaic process can occur in neutral aqueous electrolytes due to the presence on carbon surfaces of different oxygenated groups, *i.e.*, the overall capacitive behavior verified for different carbon-based electrodes is not purely capacitive neither pseudocapacitive since it involves an interplay of these different phenomena. **Table 1** shows some recent reports on SCs based on the use of oxygen-functionalized carbon materials.

As verified, the main route explored to perform the functionalization of carbon nanostructures is the chemical treatment with strong acids, which is not a green process from the environmental viewpoint. On the other hand, oxygen plasma treatment is an environmentally friendly process with the negligible generation of chemical residues that ensures controllable functionalization of the carbonaceous nanostructure, yielding materials with improved wettability, high surface area, and a surface rich in oxygenated groups with a redox activity.

Carbon material	Functionalization technique	0 (%)	$R_{\mathrm{ESR}}\left(\Omega ight)$	Capacitance	Electrode mass	Ref.
Exfoliated graphene oxide	H ₂ SO ₄ solution	-	1.30	146 F g ⁻¹	-	[104]
Incompletely reduced graphene	Reduction of graphite oxides via microwave irradiation	10.31	-	245 F g ⁻¹	-	[105]
Graphene and porous graphene	Thermal reduction in argon and oxidized by HNO ₃	13.17	1.34	$107 {\rm ~F~g^{-1}}$	-	[106]
Activated carbon	KOH activation	18.50	0.19	$280.6 \ \mathrm{F} \ \mathrm{g}^{-1}$	2 mg	[107]
Activated carbon	Oxidation using ammonium persulfate	9.75	0.7	$142 \ F \ g^{-1}$	-	[108]
Activated carbon	Electrochemical oxidation	14.8	0.1	$534 \ F \ g^{-1}$	2.5 mg cm^{-2}	[109]
Hierarchical porous carbon	KOH activation	18	-	$308 \ {\rm F} \ {\rm g}^{-1}$	-	[110]
Porous carbon (HLPC)	KOH activation	32.95	~0.44	$501 \ {\rm F} \ {\rm g}^{-1}$	-	[111]
Black carbon	Oxygen plasma	15.69	3.3	171.4 F g^{-1}	15 mg cm^2	[112]
Helical carbon nanofibers (HCNFs)	Modified Hummers method	28.03	0.72	143.6 F g ⁻¹	-	[113]
Carbon cloth	Low-temperature air activation method	8	4.96	$60.8 \ F \ g^{-1}$	16.6 mg cm^{-2}	[114]
Carbon Nanotube (CNT) fibers	Oxygen plasma functionalization	~27.5	-	20.91 F g ⁻¹	-	[115]
MWCNT and graphene composite	H ₂ SO ₄ /HNO ₃ (3:1, v/v) solution	-	0.7	$302 \ F \ g^{-1}$	0.0015 mg	[116]
Tip-open CNT	chemical-acid-etching	-	-	284 mF cm^2	-	[117]
Single Wall CNT	Arylsulfonic acid and pyrrole	12.3	-	$350 \ F \ g^{-1}$	-	[118]
MWCNT	Via aromatic azides	-	0.122	$240 \ F \ g^{-1}$	-	[119]

Table 1. Summary of the literature reports on supercapacitors based on oxygen-functionalized carbon materials.

The present work is focused on studying the overall capacitance of nanostructured carbon-based electrodes modified by a simple functionalization method (oxygen-plasma etching) to incorporate redox-active oxygenated surface groups on carbon structures. Different

ex-situ and *in-situ* studies were accomplished to evaluate the pseudocapacitance contribution of the oxygenated surface groups. Functionalized multiwalled carbon nanotubes (f-MWCNT) were used to obtain self-sustained porous buckypaper electrodes. The latter is a binder-free electrode material that retains the excellent electrical conductivity exhibited by MWCNTs, thus reducing to a minimum the equivalent series resistance (ESR) of the symmetric coin cell. In particular, a theoretical analysis is presented to understand the distributed capacitance behavior and the influence of the electrolyte resistance inside the different pores on the charge-storage process.

2. Experimental

2.1 Electrode preparation

Figure 1 outlines the MWCNT buckypaper preparation and the functionalization procedure. The buckypaper preparation was started by mixing 40 mg of multiwalled carbon nanotubes (MWCNTs) purchased from CNT Co. Ltd. (Korea) (Model: Ctube-120, 95% purity, 10–40 nm diameter, 1~25 μ m length) with 200 mL of a 0.02 mol dm⁻³ sodium dodecyl sulfate (SDS) solution as reported elsewhere [54]. The mixing was performed under sonication for 30 min at 800 W to obtain a homogeneous water dispersion. Then, the dispersed MWCNTs were slowly filtered under vacuum using a 0.22- μ m pore PTFE membrane. The samples were copiously washed and maintained in deionized water overnight to remove the SDS excess. Finally, the MWCNTs formed buckypaper sheets with *ca*. a 110- μ m thickness, as represented in **Figure 1**. The sheets were cut into 1.0 cm diameter disks for inserting in the CR2032 standard coin cell. The average buckypaper electrode mass was 3.0 ± 0.1 mg.



Figure 1. Schematic representation of MWCNTs buckypaper electrode preparation and functionalization.

The oxygen-plasma functionalization (OPF) procedure applied to MWCNT buckypaper electrodes was performed as reported elsewhere [43,44]. The optimized OPF conditions used in this work included the use of 20 cm³ min⁻¹ oxygen volumetric flow rate and application of an DC pulsed voltage of ± 1500 V at 20 kHz for 10 min.

2.2 Ex-situ characterization of the functionalized carbon material

The prepared electrodes were characterized by SEM, Raman, and XPS techniques. The morphology analysis by SEM was carried out using SEM-INSPECT FEI-50 equipment and a model Quattro ESEM microscope (Thermo Scientific). Raman spectra were recorded at room temperature using a Renishaw inVia Raman spectrometer equipped with a He-Ne laser (632.8 nm) using a 50× objective lens. The equipment was calibrated using a crystalline silicon sample. Raman spectra were deconvoluted using Lorentzian and Gaussian functions with the aid of Fityk software [120]. XPS analyses were carried out using K-alpha radiation with an X-ray Photoelectron Spectrometer (XPS) (Thermo Scientific). Spectra were deconvoluted using Gaussian functions with the Fityk software.

2.3 Electrochemical studies

The electrochemical studies were performed using a model CR2032 symmetric coin cell containing a cellulose porous separator (NKK TF4850) soaked with a 1.0 M Li₂SO₄ solution. A model VersaSTAT 3 potentiostat from PAR was employed to accomplish the cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), single-step chronoamperometry (SCA) and galvanostatic charge-discharge (GCD) experiments. The correct *working voltage window* (WVW) in the total absence of water-splitting was accurately determined using SCA and EIS experiments according to the methodology recently proposed by our research group [55]. The specific capacitance and the equivalent series resistance using the different electrochemical techniques were determined as reported elsewhere [16].

The EIS was carried out in the frequency range of 10 kHz to 10 mHz using as the *d.c.* voltage the WVW value determined previously in this work (see further discussion). A low sinusoidal signal with an amplitude of 10 mV (peak-to-peak) was used to ensure linear conditions [9,44]. Impedance findings were quantitatively interpreted using the well-known Tilak-Conway circuit model proposed for studying the behavior of the electrode/solution interface in the presence of a reversible pseudocapacitance due to the occurrence of a solid-state redox reaction coupled to the electrical double-layer capacitance process. Depending on the experimental capacitances, the circuit model permits decoupling the electrostatic and faradaic components of the overall capacitance, which is not possible using other conventional electrochemical techniques [44]. The fitting & simulation procedure using the complex nonlinear least squares (CNLS) method was carried out using the NOVA software from Metrohm Autolab. Very good simulations were verified with a relative error for each circuit's parameter of less than 3% (please see **Table 3**).

The GCD curves were performed from 0.6 to 30 mA cm⁻². The areal capacitance (F cm⁻²) of a single electrode in symmetric configuration was calculated according to Eq. 3:

$$C_{Areal} = 4 \times \frac{I}{A_t \left(\frac{dU}{dt} \right)},\tag{3}$$

where *I* is the discharging current (A), A_t is the total geometric surface area of the electrodes (cm²), and dU/dt is the slope of the GCD discharging curve (V s⁻¹).

3. Results and discussions

3.1 Ex-situ characterization studies

As-prepared and oxygen-plasma functionalized (OPF) MWCNT buckypaper materials were characterized by SEM, XPS, and Raman techniques. Figure 2 shows the SEM of (a & b) as-prepared and (c & d) functionalized materials. The top view of the samples evidence that samples had a flat carpet-like surface morphology. A closer inspection showed that the asprepared buckypaper samples have an entangled MWCNT distribution. At the same time, the OPF samples revealed a porous surface morphology containing isolated islands with several summits and valleys. Therefore, the strong electric field and ions present in the OPF treatment resulted in a very different surface morphology compared to the as-prepared carbon-based samples. A plausible explanation for these findings is an electrostatic approximation due to positive O_2^+ and negative O^- ionic adsorption and etch followed by a plasma welding due to a localized heating process [121]. We have observed similar effects elsewhere [122]. Figure 2 (d) also indicates that OPF promoted an exfoliation and opened the nanotube structures as was reported elsewhere [76,123]. Generally, the OPF buckypaper materials exhibited localized charge density distributions, as revealed by the white spots in Figure 2 (d), *i.e.*, the electron beam used in the SEM analysis concentrated the electric charge at the crest structures of the carbon sample in accordance with Gauss's law for metallic conductors.



Figure 2. SEM images from (a & b) as-prepared and (c & d) OPF MWCNT buckypapers.

It was previously reported that OPF is beneficial for the charge-transfer in electrode materials used in SCs and improves the electrode wettability, thus increasing the electrochemically active surface area, due to the incorporation of the oxygenated surface groups attached on the carbon surface [76]. It is also known that the surface concentration of the oxygenated functional groups is a function of plasma pressure, exposure time, and applied voltage [124]. Therefore, the current work has the merit of improving the OPF experimental conditions to obtain a substantial improvement of the surface and physicochemical characteristics verified for the as-prepared nanostructured carbon samples, thus improving the overall material characteristics for practical applications in SCs (see further discussion). In this sense, it is essential to check the surface composition and content of the oxygenated functional groups present on the carbon surface.

Figure 3 shows the XPS spectra from (a & b) as-prepared and (c & d) OPF MWCNT buckypaper materials.



Figure 3. XPS spectra of (a & b) as-prepared and (c & d) functionalized (OPF) MWCNT buckypaper materials, focusing on the (a & c) O1s and (b & d) C1s binding energy regions.

XPS analyses indicate that the surface oxygenated functional group was 30% after the 10 min. of oxygen-plasma treatment (Please see **Table 2** for further information). **Figure 3 (a & c)** shows the O1s binding energy region deconvoluted into three bands distributed in the 540 to 528 eV interval. These findings reveal the presence of different surface groups: C-O-C, C-O-OH, C-OH (at 535 eV), C=O (at 532.7 eV), as well the physically adsorbed oxygen (O) at 530.5 eV [76,125]. The C1s binding energy region was deconvoluted into six bands present in the 294 to 284.4 eV range. As shown in **Figure 3 (b & d)**, the latter findings are characteristic of the presence of π - π * bonds, carbonates, -O-C=O, C-O, surface defects, and the C-C bonds [123,125]. There is clear evidence that the surface concentration of different oxygenated groups (*e.g.*, C-O-C, C-O-OH, C-OH, C-OH, C-OH, O-C=O, and C-O), as well the surface defects, increased as a function of plasma exposure time. Similar findings were reported elsewhere [76,123]. In addition, the pronounced C-C signal evidenced the high quality of the MWCNTs.

Elapsed time	Atomic %	Ref.
As-prepared	2-5%	[123,124]
2 min	18-20%	[123,124]
10 min	25-30%	This work
30 min	20%	This work

Table 2. Oxygenated functional groups on the electrode surface of carbon electrodes.

Raman spectra of the carbon-based samples complement the XPS data in terms of analyzing the carbon hybridization, crystallinity, presence of functional groups, and surface defects. **Figure 4** shows the Raman spectra of (**a**) as-prepared and (**b**) functionalized buckypaper MWCNT materials. First-order Raman spectra were deconvoluted into the D, G, and D' bands that are typical for carbon-based materials. At the same time, second-order Raman spectra revealed the presence of G' and D+G bands. The G-band corresponds to the structural vibration mode (E_{2g}) occurring between the intersection branches of the iLO and iTO Raman active phonons [126–129]. D- and D'-bands are assigned to a simultaneous resonance effect at the graphene K point, related to the π electrons and the presence of phonons. The presence of punctual or edge defects gives rise to the resonance effect originating the latter Raman bands [126–129].

The G'-band is an intervalley double resonant process related to the stacking of the graphene layers, that here is affected by the characteristic multiple-wall CNT structure [44,130]. D+G bands can be ascribed to the occurrence of edge defects at the top of MWCNTs. According to Ferrari and Basko [126], this band can arise from a resonant process activated by structural defects. Nevertheless, it is important to note the existence of bands at ~1200 and ~1500 cm⁻¹. These bands are the so-called D₁- and D₂-bands, respectively, which correspond to the *sp*²-*sp*³ bonds (*e.g.*, stretching vibrations in the C–C and C=C bonds). D₁-band also indicates the presence of amorphous materials [126,131,132]. In the case of the D₂-band, it is assigned to the functional surface groups introduced by the OPF treatment process [46,124]. From **Figure 4**, a comparison between the (**a**) as-prepared and (**b**) OPF samples with a 10-min plasma exposure time revealed a redshift in the D₂-band position, which is probably related to the increased number of functional groups present in the OPF treated samples.



Figures 4. Raman spectra for (a) as-prepared and (b) functionalized (OPF) MWCNT buckypaper materials.

Analysis of the D and G bands relative intensities (I_D/I_G ratio) provided information about the Raman active defects present on the OPF functionalized MWCNTs [76,133]. An increase from 1.75 to 2.14 was verified for the I_D/I_G ratio after the OPF treatment process, revealing an increase of the edge defects due to the exfoliation of MWCNTs caused by the oxygen plasma.

In summary, our set of *ex-situ* characterization data revealed that the oxygen-plasma functionalization (OPF) treatment process effectively resulted in surface and structural changes of the MWNCT buckypaper samples by incorporation of several different oxygenated surface groups with possible redox activities and an increase in the exposed surface area (roughness factor). These surface modifications can lead to important contributions to the overall electrochemical characteristics exhibited by the carbon-based electrodes housed in the aqueous-based symmetric coin cell (see further discussion).

3.2 Electrochemical studies in symmetric coin cells

We prepared several symmetric coin cells using the as-prepared and OPF buckypaper electrodes to record CV and GCD data to compare the current-voltage response and charge-storage properties as a function of the OPF exposure time. From **Figure 5** (a), we verified a maximum increase of $\approx 15\%$ for the voltammetric charge after an OPF treatment carried out for 10 min. Accordingly, the analysis of **Figure 5** (b) revealed a concomitant increase in the specific capacitance of *ca*. 15% after the OPF treatment, calculated from GCD curve at a discharge current of 1 mA. From these initial considerations, all further electrochemical data discussed in this work refer to the OPF treatment accomplished for 10 min.

It is worth mentioning that the symmetric CV profile shown in **Figure 5 (a)** characterized by a pronounced reversible redox band centered at ≈ 0.5 V is practically identical to that previously reported by Andreas and Conway [103]. According to these authors, the origin of this redox band is the faradaic activity (*e.g.*, QH₂ \leftrightarrow Q + 2H⁺ + 2e⁻) of the quinone functionalities (Q) present at the periphery of the graphene layers.



Figure 5. (a) CV and (b) GCD data obtained from as-prepared and functionalized (OPF) MWCNT buckypaper electrodes. Conditions: symmetric coin cell containing a 1.0-M Li₂SO₄ solution.

Following a recently published protocol [55], the CV, EIS, and SCA techniques were applied in combination to correctly determine the *working voltage window* (WVW) for the symmetric coin cells in the total absence of water-splitting. **Figure 6** presents the electrochemical findings obtained for the as-prepared (**a**, **c**, **e** & **g**) and the OPF (**b**, **d**, **f** & **h**) modified buckypaper electrodes.


Figure 6. Electrochemical findings for the different symmetric coin cells. Techniques: (**a** & **b**) CV data at 100 mV s⁻¹; (**c** & **d**) SCA data at $U_c = 1.0$ V; EIS data ((**e** & **f**) complex-plane and (**g** & **h**) Bode plots) at $U_{d.c.} = 1.0$ V.

Figures 6 (a & b) show the CV data obtained at 100 mV s⁻¹ for the different symmetric coin cells. As seen, the anodic voltage limit was progressively increased in steps of 0.2 V until the maximum value was reached by the onset of the water-splitting reaction (electrolyte decomposition). We can anticipate at this point that the maximum WVW obtained for both symmetrical cells with the aid of the SCA and EIS techniques was 1.0 V.

According to the literature [55], the single-step chronoamperometry (SCA) together with the impedance method (EIS) can be used to confirm the WVW value that is commonly (roughly) estimated from the CV experiments. **Figures 6 (c & d)** shows the current transients used to detect the presence of water-splitting at 1.0 V, *i.e.*, the apparent value evaluated from the CV curves. Considering the R_{ESR} - C_{EDL} circuit model for blocked interfaces ($R_{\text{ct}} \rightarrow \infty$) impermeable to the electron transfer associated with irreversible redox reactions (*e.g.*, EDLCs), the application of the Heaviside's step function (U = 0 at t < 0, and $U = U_{\text{step}}$ at $t \ge 0^+$), where $U_{\text{step}} = WVW$, can be used to discover the true capacitive/pseudocapacitive voltage window where the electrolyte is chemically stable. Thus, considering the R_{ESR} - C_{EDL} circuit model, the measured current transient must practically disappear after a brief polarization time according to the following expression [55]:

$$I = I_0 \exp(-t/\tau), \tag{4}$$

where $(I_0 = U_{\text{step}}/R_{\text{ESR}})$ is the initial (maximum) current at $t = 0^+$, and τ is the cell's time constant $(\tau = R_{\text{ESR}}C_{\text{EDL}})$. The practical (quantitative) criterion used to rule out the presence of watersplitting is based on the relative current reduction of $\approx 99.9\%$ (*e.g.*, $I/I_0 \le 0.001$) at the end of the charging process. On the contrary, as predicted for irreversible redox reactions (Faraday's law), a *stationary current* must be verified when the water-splitting takes place.

It was observed for the applied voltage step ($U_{\text{step}} = 1.0 \text{ V}$) the presence of a residual current of 74 µA cm⁻² and 86 µA cm⁻² for the as-prepared and OPF electrodes, respectively (after $\approx 10 \text{ s}$). These findings, considering $I_0 > 90 \text{ mA cm}^{-2}$ for both devices (**Figure 6 (c & d)**), correspond to a strong relative current reduction ($\approx 99.9\%$). In this sense, the analysis of the present SCA data revealed the absence of water-splitting for the different symmetric coin cells polarized at $U_{\text{step}} \leq 1.0 \text{ V}$.

Figures 6 (e & f) shows the impedance data (complex-plane plots) obtained at $U_{d.c.} =$ 1.0 V. In the case of capacitive (blocked) electrodes and stable electrolytes, the impedance response in the complex-plane plot must be characterized by a low-frequency vertical straight line [55]. As seen, the impedance plots were indeed characterized by an almost vertical line,

revealing the presence of excellent capacitive/pseudocapacitive properties. The two insets for the different coin cells show the presence of high-frequency semicircles. The latter is due to the pseudocapacitance associated with the reversible redox-activity of the oxygenated surface groups (*e.g.*, $QH_2 \leftrightarrow Q + 2H^+ + 2e^-$) occurring in parallel to the electrical double-layer charging process (see further discussion).

In agreement with the literature [55], the vertical low-frequency data points verified in **Figures 6 (e & f)** confirm the absence of water-splitting at $U_{d.c.} = 1.0$ V. On the contrary, the complex-plane plots would be characterized by a low-frequency semicircle whose diameter refers to the charge-transfer resistance accounting for the irreversible water decomposition process.

Since both criteria proposed for the EIS and SCA techniques must be considered in the proposed protocol [55] to correctly establish the WVW values, we can affirm that the different symmetric coin cells, assembled using the as-prepared and OPF treated electrodes, did not operate under water-splitting conditions when $U_{d.c.} \leq 1.0$ V. Therefore, the oxygen–plasma functionalization (OPF) treatment did not affect the WVW of the MWCNT buckypaper electrodes, *i.e.*, the OPF treatment did not increase or reduce the capacitive voltage window. At the same time, the overall capacitance increased after the electrode treatment (see further discussion).

Analysis of the Bode plots (**Figures 6 (g & h**)) showed values for the characteristic frequencies (f_c) that were displaced from ca. 100 Hz to 10 Hz after the OPF electrode treatment, *i.e.*, the characteristic time constant ($\tau_c = 1/f_c$) increased after the oxygen-plasma treatment due to the overall capacitance increase promoted by the presence of redox-active oxygenated surface groups. According to the Tilak-Conway impedance model (*e.g.*, $R_{\text{ESR}}[C_{(\text{EDL})}/(R_{\text{ct}}C_{\text{ads}})]$), one has a *pseudocapacitive time constant* ($\tau = R_{\text{ct}}C_{\text{ads}}$), where the *adsorption pseudocapacitance* (C_{ads}) is coupled to the *charge-transfer resistance* (R_{ct}) representing the *reversible solid-state surface redox reaction* (*e.g.*, QH₂ \leftrightarrow Q + 2H⁺ + 2e⁻). In principle, the presence of well-defined semicircles in the high-frequency region indicates that $C_{\text{ads}} >> C_{\text{EDL}}$, *i.e.*, the complex-plane plot must be characterized by a high-frequency semicircle followed by a low-frequency vertical line (see **Figures 6 (e & f)** and **Table 3**).

For the symmetric cells obeying the Tilak-Conway impedance model, it can be demonstrated the impedance response is given by the following generalized admittance (*Y*):

$$Y = \frac{1}{Z} = j\omega C_{\text{EDL}} + \frac{j\omega C_{\text{ads}}}{j\omega R_{\text{ct}} + 1}$$
(5)

Tilak-Conway circuit model was slightly modified in the current work to consider the influence of frequency/capacitance dispersion. Thus, the conventional capacitances (C_{EDL} and C_{ads}) were substituted by constant phase elements (CPE), whose impedance is given by $Z_{CPE} = 1/Y_0(j\omega)^n$, where $n \approx 1$ for well-behaved SCs and PCs. In this sense, we used the circuit $R_{ESR}[Y_{0(EDL)}/(R_{ct}Y_{0(ads)})]$) to simulate the impedance data using the complex non-linear least squares (CNLS) method. The following elements are present in the impedance model: (*i*) equivalent series resistance (R_{ESR}) representing the overall ohmic behaviour of SCs, (*ii*) electrical double-layer capacitance ($Y_{0(EDL)}$) representing the electrostatic contribution to the overall charge-storage process, (*iii*) adsorption pseudocapacitance ($Y_{0(ads)}$) involving the chemical behaviour of the reversible solid-state surface redox reaction, and (*iv*) charge-transfer resistance (R_{ct}) describing the electron transfer. Very good simulations of the impedance findings were obtained with very small relative errors (< 3%) for each circuit parameter.

The values of the areal capacitances (*C*/F cm⁻²) obtained for individual (single) electrodes were extracted from the Y_0 simulation parameters having a fractal dimension (Y_0 /F s^{*n*-1} cm⁻²) using the well-known Brug-Sluyters' formula [134,135]:

$$C = 4 \left(Y_0 \right)^{1/n} \left(\frac{1}{R_{\text{ESR}}} + \frac{1}{R_{\text{ct}}} \right)^{1 - 1/n}, \tag{6}$$

where R_{ESR} is the equivalent series resistance (Ω cm²), R_{ct} is the charge-transfer resistance (Ω cm²), and *n* is the CPE's exponent. The multiplication factor of 4 is used to express the result for a single electrode.

 Table 3 gathers the EIS simulation findings for the as-prepared and OPF treated
 electrodes obtained using the Tilak-Conway's impedance model.

Analysis of **Table 3** revealed R_{ESR} values for the different electrodes in the *ca*. 0.8–2.9 Ω cm² range. These findings are consistent with the electronic properties exhibited by MWCNTs and the use of well-designed coin cells. It was observed that $n \ge 0.88$, which is consistent with the use of porous/rough electrode materials. The low-frequency pseudocapacitive behavior was characterized by almost negligible dispersive effects ($n \ge 0.95$). These findings also corroborate the absence of water-splitting in the different coin cells. Data obtained for the electrical double-layer (*e.g.*, electrostatic process) revealed a $\approx 25\%$ capacitance increase after the OPF treatment process. The latter findings are mainly due to an increase in surface roughness incurred by the OPF treatment process (see the SEM images in **Figure 2**). On the contrary, only a minor pseudocapacitance variation of $\approx 0.5\%$ after the OPF

treatment process was observed, *i.e.*, most of the oxygenated surface groups incurred from the OPF process are not electrochemically active. Therefore, we can affirm that the major influence of the OPF treatment process was on the roughness factor governing the surface morphology characteristics instead of the surface concentration of the redox-active species.

Despite these considerations, one has the major contribution to the *total capacitance* $(C_{\text{total}} = C_{\text{EDL}} + C_{\text{ads}})$ for the different symmetric devices was given by the pronounced redox-activity of the oxygenated surface groups present in the different electrodes.

Buckypaper electrode	Element	Value	Relative error	C (non-fractal)
As-prepared MWCNTs	$R_{ m ESR}$	$0.8 \ \Omega \ cm^2$	2.9%	
	$R_{ m ct}$	$4.5 \ \Omega \ cm^2$	0.8%	
	$Y_{(0)\text{EDL}}$	55 μ F s ^{<i>n</i>-1} cm ⁻² (<i>n</i> = 0.90)	1.9%	$C_{\rm EDL} = 234 \ \mu {\rm F} \ {\rm cm}^{-2}$
	$Y_{(0) m ads}$	9 mF s ⁿ⁻¹ cm ⁻² ($n = 0.97$)	0.6%	$C_{\rm ads} = 38.1 \ {\rm mF \ cm^{-2}}$
Functionalized MWCNTs	$R_{ m ESR}$	$2.9 \ \Omega \ cm^2$	1.9%	
	$R_{\rm ct}$	$17.1 \ \Omega \ cm^2$	1.1%	
	$Y_{(0)\text{EDL}}$	73 μ F s ^{<i>n</i>-1} cm ⁻² (<i>n</i> = 0.88)	2.0%	$C_{\rm EDL} = 593 \ \mu { m F} \ { m cm}^{-2}$
	$Y_{(0) m ads}$	9.02 mF s ^{$n-1$} cm ^{-2} ($n = 0.95$)	1.0%	$C_{\rm ads} = 42.5 \text{ mF cm}^{-2}$

Table 3. EIS findings obtained using the Tilak-Conway's model. Electrolyte: 1.0 M Li₂SO₄.

As can be seen, the *adsorption pseudocapacitance contribution* occurred in the mF cm⁻² range while the *electrostatic contribution* was verified to occur in the μ F cm⁻² interval, *i.e.*, in practice, one has that $C_{\text{total}} \cong C_{\text{ads}}$. Therefore, it was possible to identify unambiguously the fundamental contribution of the pseudocapacitance to the overall charge-storage characteristics of carbon-based SCs. These findings reinforce the vital influence of pseudocapacitance on the overall characteristics of EDLCs.

Finally, an increase by a factor of ~ 4 was verified for R_{ct} . In principle, this result indicates a negative impact on the reversible nature of the solid-state redox reactions caused by the OPF treatment process. Since the roughness factor increased after the OPF treatment, it can be proposed that the chemical nature (degree of reversibility) of the active redox sites changed due to an increase in the activation barrier for electron transfer.



Figure 7. Galvanostatic discharge curves (a & b), specific capacitance, and ESR values (c & d), respectively, as a function of the gravimetric current, and the (e) cycling stability (floating time) test.

Figures 7 (a & b) and **7 (c & d)** show the discharging curves and the areal capacitance and ESR values, respectively. **Figure 7 (e)** presents the cycling stability test of the as-prepared and OPF electrodes performed in a floating time experiment using 1.0 V for 10 h. It was verified that the specific capacitance of as-prepared electrode has retained 99.6% of its initial specific capacitance after 10 h and the OPF electrode has retained 98.9%, presenting good stability.

As verified, the discharge curves are not strictly linear as expected for ideal EDLCs. In principle, the concave shape of these curves indicates the presence of a *distributed capacitance* in the time domain incurred by the presence of hierarchically interconnected pores with different time constants ($\tau = R_{pore}C_{pore}$). In these cases, as the solution resistance inside the pores increases for narrow and deep pore structures (*e.g.*, $R_{pore} = \rho_{pore}(L_{pore}/A_{pore})$ – see further discussion), the distributed *RC* values inside the *inner surface regions* also increase, resulting in a more sluggish charge-storage process [103].

3.2.1. Theoretical basis for the distributed capacitance verified in the SCA experiments and the influence of the pore resistance on the charge-storage process

In principle, the electrochemical response referring to the *inner* and *outer* surface regions can be accessed using the *single-step chronoamperometry* (SCA) technique. In this sense, the total electrochemically active surface area (A_{total}) is given as:

$$A_{total} = A_{in} + A_{out}, \tag{7}$$

where A_{in} and A_{out} are the '*inner*' and '*outer*' surface regions present in porous electrodes [136].

According to Helmholtz's model valid for the electrical double-layer in concentrated electrolytes, one has the electrical double-layer capacitance linearly scales with the electrochemically active surface area ($C = \varepsilon_0 \varepsilon A/d$). Therefore, the effect of the *inner* and *outer* surface regions appears as *two capacitors connected in parallel* [136,137]:

$$C_{total} = C_{in} + C_{out} \tag{8}$$

Considering that $C \equiv dQ/dU$ and $I \equiv dQ/dt$:

$$I_{total}\left(\frac{dt}{dU}\right) = I_{in}\left(\frac{dt}{dU}\right) + I_{out}\left(\frac{dt}{dU}\right)$$
(9)

Since the voltage changes are equal for the *inner* and *outer* surface regions behaving like two capacitors connected in parallel, we can differentiate both sides of Eq. (9) in relation to time to obtain the current distribution in the different porous electrode regions. In this sense, the *total capacitive current* (I_{total}) flowing in the porous electrode structure is:

$$I_{total} = I_{in} + I_{out} + I_{res}, \qquad (10)$$

where I_{res} is an additional term designated as the residual (background) current. The latter is inherent to most SCA experiments since, from the theoretical viewpoint, a zero capacitive current could only be achieved at $t \rightarrow \infty$. In addition, the presence of parasitic (side) reaction also restricts to attain zero-current values in practical cases unless extremely purified solutions are used.

Using Eqs. (4) & (10), the distributed transient current is given as follows:

$$I_{total} = I_{0(in)} \exp(-t/\tau_{in}) + I_{0(out)} \exp(-t/\tau_{out}) + I_{res}, \qquad (11)$$

where $\tau_{in} = R_{in}C_{in}$ and $\tau_{out} = R_{out}C_{out}$ are the respective time constants for the *electrochemically* accessible pores. R_{in} and R_{out} are the *specific pore resistances* ($\Omega \text{ cm}^2$) incurred by the electrolyte presence inside the pores (De Levie's model). In practical cases, these resistances also include the contribution from the *equivalent series resistance* (R_{esr}), although we commonly have that $R_{pore} \gg R_{esr}$ [137]. The pre-exponential factors in Eq. (11) are $I_{0(in)} = \delta U/R_{in}$ and $I_{0(out)} = \delta U/R_{out}$, where δU (= 1.0 V) is the applied voltage-step used in the SCA experiments.

Quantitatively, the *pore accessibility* is governed by the *pore resistance* (R_{in} and R_{out}). In principle, the latter can be evaluated from the general electrostatic model analysis based on Eq. (11). In this sense, we have the *total charge* (Q_{total}) stored at the electrode/solution interface in the presence of pore resistance is given as follows:

$$Q_{total} = \int_{0}^{t} I_{total} dt = I_{0(in)} \int_{0}^{t} \exp(-t/\tau_{in}) dt + I_{0(out)} \int_{0}^{t} \exp(-t/\tau_{out}) dt + \int_{0}^{t} I_{res} dt$$
(12)

Integration of Eq. (12) yields the relationship describing the transient behavior of the asymptotic charge accumulation at the electrode/solution interface affected by pore resistance:

$$Q_{total} = I_{0(in)} \tau_{in} [1 - \exp(-t/\tau_{in})] + I_{0(out)} \tau_{out} [1 - \exp(-t/\tau_{out})] + Q_{res}$$
(13)

The distinct non-linear terms in the brackets of Eq. (13) can be linearized considering a first-order approximation of the exponential function $(e.g., \exp(-t/\tau) \cong 1 - t/\tau, \text{ if } t/\tau \ll 1)$. This linearization can be achieved in practice using appropriate time intervals in the SCA experiments where the individual t/τ ratios can be made as low as possible.

From these considerations, the dynamics of the charge-storage process in porous electrodes is described by the following linear equation:

$$Q_{\text{total}} \cong Q_{\text{res}} + (I_{0(\text{in})} + I_{0(\text{out})}) \times t, \qquad (14)$$

where $R_{pore} = \delta U/I_{0.}$

On the contrary, since $\tau_{in} \gg \tau_{out}$, one has after considering a relatively short polarization time that $I_{0(in)} \ll I_{0(out)}$. This case represents the difficulty imposed for ions to access the *inner surface regions* mainly composed of deep/narrow micropores. As a result, at relatively reduced times, *i.e.*, $t \le \tau_{out}$, only the shallow/large meso- and macro-pores can be rapidly accessed by the electrolyte species, as represented by Eq. (15):

$$Q_{total} \cong Q_{res} + I_{0(out)} \times t \tag{15}$$

Therefore, one can construct a generalized plot (Q vs. t) to discriminate from the slopes (dQ/dt) the individual specific pore resistances (R_{in} and R_{out}).

Figure 8 (a & b) shows the nonlinear curve fitting analyses accomplished for the different carbon-based electrodes using the model described by Eq. (13). As can be seen, very good simulations ($\chi^2 \approx 10^{-9}$) can be obtained supporting the assumption that the overall electrode response in the time domain is characterized by the existence of two time constants referring to the *outer* and *inner* surface regions. The numeric values of the different parameters referring to the *inner* and *outer* surface regions incorporated in I_0 and τ are gathered in **Table 4**.

In the case of the as-prepared electrodes, considering the fitting parameters of the curve in **Figure 8 (a)**, we obtained areal capacitances of 6.2 and 4.6 mF cm⁻² for the *outer* and *inner* surface regions, respectively. These capacitances correspond to a Morphology Factor ($\Phi \equiv C_{in}/(C_{in} + C_{out})$) of 42% [136]. At the same time, the values obtained for the OPF modified electrodes (**Figure 8 (b)** curve) were 10 and 4.8 mF cm⁻² for the *outer* and *inner* surface regions, respectively, yielding an Φ -value of 32%.

These findings reveal that the *outer surface regions* govern the charge-storage process observed for both electrodes (*e.g.*, $\Phi < 50\%$). The device's slight change in the *inner capacitance* against the significant *outer capacitance* increase shows that the functionalization promotes better accessibility to the electrochemically active areas related to the *outer surface regions*. This may be related to the well-known superhydrophilic behavior of CNTs after functionalization [124]. Therefore, the dynamics accounting for the ionic accessibility inside the meso- and macro-pores can be vital to the overall charge-storage characteristics in EDLCs.

Buckypaper electrode	Variable	Value
	Q_{res}	190 µC
	$I_{0(in)} au_{in}$	7.2 mC
	$I_0(out) au_{out}$	9.7 mC
As-prepared MWCNTs	$ au_{in}$	0.258 s
	$ au_{out}$	0.047 s
	Slope θ_1	200 mA
	Slope θ_2	16 mA
	Q_{res}	160 µC
	$I_{0(in)} au_{in}$	7.6 mC
Functionalized	$I_0(out) au_{out}$	16 mC
MWCNTs	$ au_{in}$	0.738 s
	$ au_{out}$	0.153 s
	Slope θ_1	92 mA
	Slope θ_2	6.8 mA

Table 4. Data from the SCA analysis using the distribution capacitance model containing two different time constants.

Figure 8 (c & d) shows the experimental Q vs. t plots obtained for the as-prepared (**a**), and OPF modified (**b**) carbon-based electrodes with two linear fitting comprising the pore resistances R_{out} and R_{in} (see Eqs. (14) & (15)). As seen in **Figure 8 (c)**, the as-prepared electrodes exhibited two slopes corresponding to specific pore resistances of 7.8 Ω cm² and 98 Ω cm², for the *outer* and *inner* surface regions, respectively. This behavior is theoretically predicted for porous electrodes composed of hierarchically interconnected pores with different sizes distributed in the different surface regions. The $I_{0(out)}$ -values of 206 and 200 mA obtained from the nonlinear and linear regressions analysis, respectively, support the use of Eq. (15). The R_{out} value of 7.6 Ω cm² calculated from the nonlinear regression analysis indicates that the as-prepared electrode is mainly composed of *outer surface pores* with similar sizes, roughly characterized by a single time constant for $t \leq \tau_{out}$, validating the use of the linearized model represented by Eq. (15). On the contrary, the *inner surface pore* resistance calculated from the non-linear and linear and linear surface pore for the surface pore analysis was 56 Ω cm². The discrepancy between the non-linear and linear

regression data indicates that *R_{in}* changes during the charge-storage process due to the presence of interconnected internal (micropores) pores with different accessibilities.

The OPF modified electrodes also exhibited two well-defined straight lines in the Q vs. t plot (**Figure 8 (d)**). From the nonlinear fit, specific resistances of 15 Ω cm² and 152 Ω cm² were verified for the *outer* and *inner* surface regions, respectively. The linear fit results in R_{out} $= 17 \ \Omega \ \text{cm}^2$ and $R_{in} = 231 \ \Omega \ \text{cm}^2$. Again, similar values were obtained for R_{out} using the nonlinear regression and the linear approximation. On the contrary, a discrepancy was verified for the inner pore resistance obtained using the different regression analyses by the motif already explained above.

Considering the nonlinear fit data, one can notice that the pore resistance R_{in} increases by a factor between 7 and 10 compared to R_{out} , for both electrodes. These findings represent the resistance increase when the ionic species transited from macro- and meso-pores to micropores. Actually, the relative magnitude of the different ohmic resistances ($R_{ESR} < R_{out} < R_{in}$) complies the Clausius'law for electrolytic solutions:

$$R = \rho \times (L/A), \tag{16}$$

where ρ is the electrolyte electrical resistivity (Ω m), *L* is the length path (m) in the porous region, and *A* is the associated cross-sectional area (m²).

The classical concept of *solution resistance* (R_S) in the electrochemical experiments only considers the ohmic drop between the tip of the reference electrode and the surface of a plane or spherical working electrodes. In the present study, the solution resistance is restricted for the electrolyte confined in the porous separator, *i.e.*, the influence of the electrolyte resistance inside porous electrode structures is not considered. From the EIS analyses, the R_S value is usually obtained at *ca*. 10–100 kHz. In other words (as t = 1/f), the R_S arises from a "*time constant*" about 1000 times smaller than τ_{out} , *i.e.*, the solution resistance is unrelated to the electrolyte behavior inside different pores present in the electrode material. Thus, to a first approximation, Eq. (16) might be applied considering the pertinent L/A-ratios: $(L/A)_{separator} \ll$ $(L/A)_{outer-pores} \ll (L/A)_{inner-pores}$. However, it is not guaranteed that ρ is the same for the different pore structures.

The *equivalent series resistance* (ESR) measured in several previous works does not account for the electrolyte resistance inside the porous electrode structure. This resistance is exclusively obtained in two-electrode cells in the absence of a standard reference electrode, *i.e.*, the counter electrode is used as a pseudo-reference for the cell voltage. As a result, different ohmic components present in the entire cell are lumped in the ESR value.

These results also imply that the V_{drop} verified in the GCD discharge curves, used to calculate R_{ESR} values in **Figure 7 (c & d)**, only considers the ohmic components in the absence of pore influence. Generally, the determination of ESR values becomes less accurate at lower GCD currents [138].



Figure 8. Integrated single-step chronoamperometry (SCA) data using Eq. (13) for the different symmetric coin cells (a & b). The linear (Q vs. t) profiles for the different electrodes are shown in (c & d). Conditions: $\delta U = 1.0$ V. The distributed capacitance obtained from the GCD data are shown in (e) and (f) for the as-prepared and OPF modified electrodes, respectively.

3.2.2. Analysis of the distributed capacitance obtained from the GCD data

From the above considerations, when an SC device is charged rapidly, it is possible that ions from the electrolyte do not respond properly to the applied voltage due to the distributed porous structures with different electrolyte accessibilities. Accordingly, the presence of solidstate surface redox reactions requires a longer time during polarization since they commonly involve the diffusive transport of hydrated protons (*e.g.*, $QH_2 + 2H_2O \leftrightarrow Q + 2H_3O^+ + 2e^-$). Therefore, the determination of the "*distributed capacitance*" from the GCD experiments is very important for the analysis of the charge-storage dynamics in carbon-based SCs.

The *distributed capacitance* relationship ($C_{dist.}$ vs. t) can be experimentally accessed from the discharging curves using a derivative analysis:

$$C_{\text{distr.}} = \frac{dQ}{dU} = \frac{I}{dU/dt},$$
(17)

where I = dQ/dt, and dU/dt is the derivative (*numeric differentiation*) of the discrete available data.

Figure 8 (e & f) shows the distributed capacitance obtained for the different symmetric coin cells. As seen, there are two different plateaux for capacitance. Generally, the presence of an S-shape curve connecting the minimum and maximum distributed capacitance values indicates a change in the charge-storage mechanism as a function of the polarization time. In this sense, while the distributed capacitance profile at short polarization times indicates a similar charge-storage mechanism for the different electrodes, one has that at longer polarization times, a slow charge-storage process occurs until the maximum capacitance value is reached. In the case of the OPF modified electrodes, a more pronounced sigmoidal (S-shape) behavior was verified with a maximum distributed capacitance of *ca*. 70 mF cm⁻². In the latter case, the presence of a second plateau is not evidenced despite the asymptotic nature of the distributed capacitance.

The first capacitive plateau ($C_{\text{dist}} \approx 35 \text{ mF cm}^{-2}$) verified at relatively short times ($t \leq 0.3 t/t_{max}$) is practically identical for the different electrodes. In principle, these findings refer to the charge-storage process occurring in the *outer* surface regions. On the contrary, the second plateaux verified after ~ 0.6 t/t_{max} is more developed for the as-prepared buckypaper electrodes and corresponds to an almost constant distributed capacitance of *ca*. 50 mF cm⁻². In this case, the distributed capacitance corresponds to the charging process involving the *inner* surface regions.

A comparison of the electrochemical data obtained using different (CV, EIS, SCA, and GCD) techniques revealed that the particular timescale inherent to each experiment can be useful to understand the complexity of the charge-storage process exhibited by different porous carbon-based electrodes. The CV technique is particularly useful for an initial evaluation of the capacitive voltage interval where the electrolyte is stable, as well as the presence of solid-state faradaic processes characterized by the presence of redox bands. In particular, the EIS technique can be quite useful to discriminate the individual contributions exhibited by the electrostatic capacitance and pseudocapacitance in the frequency domain. On the other side, the use of SCA and GCD can be necessary to access the capacitance distribution in the time domain and the influence of the ionic resistance inside the different pores on the overall charge-storage process.

4. Conclusion

This work reports on the effect of oxygen functional groups on the MWCNTs surface and its consequence on electrode material performance in an aqueous-based supercapacitor. Our findings show that plasma treatment exfoliated MWCNT increasing defective areas at the external interface and bringing them together by electrostatic forces, forming mountain and valley structures in the buckypaper top surface. Surface oxygenated functional groups increased from ca. 2 to 30% after the plasma treatment. However, the reversible solid-state redox reaction (e.g., $QH_2 \leftrightarrow Q + 2H^+ + 2e^-$) only increased by *ca*. 10%. Therefore, several surface groups are electrochemically inactive. The charge-storage mechanism in the time domain and the individual contribution of the pseudocapacitance in the frequency domain were studied to clarify the real electrochemical behavior exhibited by the porous carbon-based electrode materials. It was verified that the distinct timescales assessed using different electrochemical techniques might be used to understand the charge-storage behavior from different experimental perspectives. In this sense, a deep understanding of the true electrochemical behavior exhibited by the carbon-based porous electrodes can only be achieved from a unified rational analysis obtained from the experiments using different techniques. A theoretical model was proposed to represent distributed capacitance behavior affected by the electrolyte resistance inside the different porous structures. A comprehensive discussion was presented regarding the influence of the pore characteristics on the dynamics accounting for the charge-storage process.

Chapter 3

In situ Electrochemical and operando Raman spectroscopy investigation of T-Nb₂O₅ for pseudocapacitors

Abstract

Niobium oxide (Nb₂O₅)-based electrochemical energy storage devices have stood out on the global clean energy scene. In this research work, orthorhombic Nb₂O₅ (T-Nb₂O₅) were combined with multiwalled carbon nanotubes (MWCNTs) in a buckypaper-type electrode and explored as an electrode material for Li-ion pseudocapacitors in asymmetric configuration with a buckypaper-type active carbon (AC) electrode. The *ex situ* characterization of the materials was performed by morphological, chemical, and structural analysis, including SEM, Raman and XRD, while *in situ* measurements of cyclic voltammetry, charge-discharge curves, and electrochemical impedance spectroscopy. *Operando* Raman spectroscopy was applied to help understand the energy storage mechanism, evaluating the structural changes while recording the charge and discharge curves. High specific capacitance and energy & power densities were achieved. The combination of the characteristics of MWCNTs (large voltage window and chemical stability), AC (high surface area), and T-Nb₂O₅ (facilitated intercalation of Li⁺) resulted in a high-power density pseudocapacitor with high stability.

Keywords: intercalation pseudocapacitor; asymmetric configuration; energy storage; Niobium, MWCNT, buckypaper.

1. Introduction

The growing global demand for energy, in contrast to the risk of depletion of fossil energy sources and constant warnings about climate changes associated with the consumption of this energy source, imposes significant pressure on the search for alternative, renewable and sustainable energy sources. Already consolidated in various day-to-day applications, electrochemical energy storage and conversion devices (EESCs) currently find a more favorable scenario for scientific and technological development, considering the technical aspects of safety, sustainability, and linked market to these technologies. Conventional Li-ion batteries (LIBs) and supercapacitors (SC) are widely used in portable electronic devices, electric vehicles, and hybrid vehicles. LIBs and SCs have complementary performance characteristics. While LIBs provide high energy density, SCs tend to have a longer working lifetime and quick charge/discharge, delivering high power density and long-term cycle life.

The Li-ion solid-solution intercalation in niobium pentoxide (Nb₂O₅) was first observed in 1981 [139] and its exceptional behavior as high-rate electrochemical energy storage, specifically the orthorhombic Nb₂O₅ (T-Nb₂O₅), was later reported [140,141]. The Li⁺ intercalation pseudocapacitance, as called by Conway [14,142], was established as an electrode electrochemical with a signature closely to a supercapacitor but not arising from the nonfaradaic process. In a nutshell, a supercapacitor or double-layer capacitor (EDLC) is a highpower device typically capable of more than 500,000 (five hundred thousand) cycles. A pseudocapacitor can be redox (like Ruthenium oxide in acid media) or intercalation (like T-Nb₂O₅ regarding Li⁺ ions). In this context, the supercapacitor limits are an open and vital discussion since such electrodes can be assembled in hybrid configurations [19,90,143–145].

Other materials besides the orthorhombic Nb₂O₅ and with high power capabilities have also been studied, especially in hybrids configuration with double-layer materials, like activated carbon (AC). However, there is no consensus regarding the nomenclature and even about the electrochemical characteristics of these devices (*i.e.*: in full cell configuration). Some authors propose or use the terms *Lithium-ion Capacitor* [146,147], *Supercapattery* [148], *Oxide Supercapacitors* [145], *Hybrid Capacitors* [7], among others, to refer to this type of device.

In addition to electrochemical methods, an *operando* investigation is faced. The crystal structure of T-Nb₂O₅ is complex. Thus, investigating the charge storage mechanism of a pseudocapacitive T-Nb₂O₅ electrode using *operando* Raman spectroscopy is a challenging task. Its structure consists of a sheet of Nb atoms parallel to (001) surrounded by 6 oxygen atoms forming a tilted/distorted octahedral (NbO₆) or 7 oxygen atoms forming a pentagonal bipyramidal structure (NbO₇) [149]. These polyhedral shares corners and edges, constituting an orthorhombic structure (point group D_{2h}) [149]. It is claimed that mostly empty octahedral sites between (001) planes provide natural tunnels for lithium-ion transport throughout the a-b planes [150]. This effect can depend on the structural changes induced by lithium, as in typical anode materials for lithium batteries [151].

A better understanding of the electrochemical and structural data in a prototype device in a two-electrode configuration is essential for improving the electrochemical performances of the supercapacitor technology and the knowledge about hybrid configurations, which is one of the aims of the present work.

2. Experimental procedure

2.1 Electrodes preparation

The buckypaper (BKP) electrodes were prepared according to the method commonly used in the literature [54,152]. *Multiwalled carbon nanotubes* (MWCNTs, diameter: 10-40 nm, length: 1-25 μ m, purity of 95% from CNT Coreat Co. Ltd) and T-Nb₂O₅ (99.8% purity, particles with ~2 μ m; from *Companhia Brasileira de Metalurgia e Mineração*, CBMM) were mixed in a 200 mL of a 0.02 mol dm⁻³ *sodium dodecyl sulfate* (SDS) solution prepared in deionized water containing 15 mg of each powder. The niobium oxide material was produced with a calcination step at 900°C, so it is plentiful in the orthorhombic phase but also presents about ~25% of the monoclinic phase. The mixture of MWCNTs and T-Nb₂O₅ was sonicated for 30 min. until a homogeneous dispersion was formed. The homogeneous dispersion of MWCNTs and T-Nb₂O₅ was slowly filtered using vacuum filtration through a PTFE membrane (pores with 0.22 μ m) from Millipore. Finally, the samples were washed several times with deionized water to remove SDS excess and dried in a vacuum oven for 24h at 80 °C. Similarly, using activated carbon (AC) Kuraray 80F and MWCNTs, its was prepared a 1:1 weight ratio buckypaper (40 mg total). After dried, the electrodes were cut into 1.0 cm diameter. The average electrode mass was 2.5 \pm 0.1 and 4.0 \pm 0.1 mg for T-Nb₂O₅ and AC buckypaper, respectively.

2.2 Material characterization

The morphological profile of the as-prepared BKPs based on T-Nb₂O₅ and MWCNTs (T-Nb₂O₅@BKP electrode) and AC with MWCNTs (AC@BKP electrodes) was accessed by Scanning Electron Microscopy (SEM) using a SEMI FEI-200 Nanolab microscopy (secondary electron detector with voltages between 5 and 30kV). X-ray diffraction was performed using a Philips Analytical X-Ray diffractometer with Cu-K α radiation ($\lambda = 1.5418$ Å) in a Bragg–Brentano θ/θ configuration (Goniometer PW3050/10) for investigation of the crystalline nature of the microparticles. The diffraction patterns were collected with steps of 0.01° and an accumulation time of 0.6 s per step within the range of 10°–60° (2 θ).

Raman spectra were recorded using a Renishaw inVia spectrometer equipped with a He-Ne laser (632.8 nm). The equipment was calibrated using monocrystalline silicon (band at 520.5 cm⁻¹). The spectra were collected at room temperature (23 °C) through a 50× objective of ~0.9 mm focal length and power ranging from 300 μ W to 1.5 mW (measured using a Thorlabs S120C power meter). Fityk [120] and Origin software were employed to normalize, decompose and collect the band intensities.

2.3 Electrochemical studies

The electrochemical behavior of the T-Nb₂O₅@BKP electrode was studied in asymmetric (T-Nb₂O₅@BKP asymmetric) configurations using a *coin-cell* (CR2032) for twoelectrode and an EL-CELL for three-electrode configuration. This device was compared with a symmetric one consisting of two AC@BKP electrodes. The asymmetric configuration had a T-Nb₂O₅@BKP electrode as negative and an AC@BKP as a positive electrode. The electrolyte was 1 M LiTFSI (Sigma-Aldrich) prepared in acetonitrile, and the separator was a cellulose NKK TF4850 (~ 16 mm in diameter). **Figure 1** displays the schematic assembly of the asymmetric device mounted inside an argon-filled glovebox (ppm O₂ < 2.0). The three-electrode configuration used a silver wire (Ag) of 0.3 mm diameter as pseudoreference. The EL-CELL was dried using a vacuum oven at a temperature of 80 °C for 24h and then assembled inside the glovebox.

Figure 1. Schematic representation of the coin-cell assembly in an asymmetrical configuration.

To further evaluate the electrochemical responses of these two devices, a Princeton Applied Research model VersaSTAT 3 potentiostat and a Biologic cycler model BCS-805 were used to carry out the measurement with the following electrochemical techniques: *Cyclic voltammetry* (CV), *Galvanostatic charge and discharge* (GCD), *Chrono-amperometry* (CA)

and *Electrochemical impedance spectroscopy* (EIS). The best *working voltage window* (WVW) was determined by the correlation between CV, EIS, and CA [55]. The CVs were recorded in the scan rate range of 5 to 100 mV s⁻¹ and GCD curves at gravimetric currents of 0.1 to 2 A g^{-1} , both using the best WVW of 2.5V (please further discussion). The EIS was carried out at 1kHz to 10mHz in the WVW of 2.5V with an amplitude of 10 mV (peak-to-peak).

The gravimetric capacitance C was determined for the symmetric (EDLC) and asymmetric pseudocapacitive (PC) devices applying Equation 1 [9]:

$$C = \frac{I}{m \cdot (dV/dt)} \tag{1}$$

where *I* is the galvanostatic current (ampere, A); dV/dt is the voltage variation as a function of time of the galvanostatic discharge curve (V·s⁻¹); *m* is the electrode active material mass in grams (g); and *C* is the gravimetric capacitance in Farad per gram (F·g⁻¹).

For the of energy (E) and averaged power (P) densities calculations, Equations 2 & 3 were applied, respectively [153]:

$$E = I \int_{0}^{t} V(t) dt \times \frac{10^{3}}{3600}$$
(2)

$$P_{med} = \frac{E}{\Delta t} \tag{3}$$

where *I* is the galvanostatic discharge constant current (A g⁻¹); *V* is the voltage variation of the galvanostatic discharge curve (V); *E* is the energy density (Wh·Kg⁻¹); and *P* is the average power density (W·Kg⁻¹), and Δt is the GCD interval time.

Regarding *E* and *P_{med}*, a supercapacitor can be considered discharged at the operating potential of WVW/2, *i.e.*, when 75% of its charge capacity has been delivered [14]. The energy of an ideal capacitor $E = \frac{1}{2}CV^2$ ensures that most of its energy is at higher potentials. In addition, the intercalation in the T-Nb₂O₅@BKP asymmetric device occurs at potentials around 1.2V (please see further discussion). Thus, to grant a reliable comparison, we consider WVW/2 in the *E* and *P_{med}* for both devices, symmetric AC@BKP and the asymmetric T-Nb₂O₅@BKP one.

The mass ratio between an asymmetric device's negative and positive electrodes is vital because different electrode materials exhibit distinct individual capacities [154,155]. Thus, a balance ($Q_{negative} = Q_{positive}$) is required between the two electrode charges. The mass ratio and

charge of each electrode (negative intercalation pseudocapacitance and positive EDLC) were estimated according to equation:

$$Q_{electrode} = \frac{\int_{0}^{0} I(t)dt}{m},$$
(4)

where *m* is the electrode mass (g) and *Q* is the specific capacity (mC g^{-1}).

Although one of the electrodes has a capacitance (F g^{-1}), the charge stored in the intercalation pseudocapacitance type electrode is best treated as a capacity (please see further discussion), calculated in mC g^{-1} or mAh g^{-1} to ensure proper mass in both the electrodes [143,147]. Moreover, different scan rates result in different capacities for these electrodes. In this sense, 10 mV s⁻¹ (~ 2 min. charge) was used to estimate the charge balance, usually between ~10 s up to 10 min. [156]. It is important to note that there is still no consensus on the most appropriate mass ratio for this type of device [147].

2.4 Raman operando procedure

The Raman *operando* studies were carried out with the T-Nb₂O₅@BKP electrode in an asymmetric configuration using an EL-CELL cell to carry out the measurements under operating conditions. The cell assembly is already reported elsewhere [157]. The cell was dried using a vacuum oven for 24 hours at 80 °C. The T-Nb₂O₅@BKP electrode was mounted as a negative electrode inside a glove-box (argon) in a two-electrode configuration with 1 M LiTFSI (Sigma-Aldrich) dissolved in acetonitrile as electrolyte. In this montage, a cellulose separator and an AC@BKP electrode were used, both with a concentric hole in the middle ~2 mm.

Figure 2. Schematic representation of the Raman operando analysis: (i) potentiostat, (ii) Raman spectroscope, and (iii) cell used (EL-CELL).

A Biologic SP-200 potentiostat was used for electrochemical measurement and a Renishaw Raman spectroscopy to collect the spectra using a 633 nm wavelength laser. Which spectra are taken during cyclic voltammetry between 0 V to 2.5 V at 1 mV s⁻¹ scan rate. Thus, each spectrum was acquired in a potential interval of ~0.14 V.

3. Results and discussions

3.1 Physical and chemical characterization studies

The morphological features of the different synthesized BKPs were accessed from SEM analysis. **Figure 3** shows a set of SEM micrographs recorded to the as-prepared AC@BKP and T-Nb₂O₅@BKP. As a standard feature, MWCNTs were incorporated at the BKP composition of all electrodes. Thus, the presence of MWCNTs is directly verified by visualizing tangled tubes/wires. In the case of AC@BKP, the MWCNTs are embedded in the AC, filling the gaps between the AC microparticles (Please see **Figure 3 (a &b)**).

On the other hand, the preparation of BKP from the dispersion combining T-Nb₂O₅ and MWCNTs provides non-regularly sized Nb₂O₅ particles approximately well spread over the MWCNTs. The relative non-uniformity of T-Nb₂O₅ particle size is expected considering the physical ultrasound process used to disperse the materials. However, it should be noted that the final material contains the T-Nb₂O₅ particles closely connected with hundreds of conductive MWCNTs, contributing to improving the electrical conductivity of T-Nb₂O₅, a usual drawback for Nb₂O₅-based electrodes. Additionally, the characteristic of T-Nb₂O₅ particles spread over MWCNTs is interesting to ensure the free access condition of Li electrolyte solution to T-Nb₂O₅ particles.

Kuraray activated carbon has a high surface area (~2100 m² g⁻¹) (data from datasheet) and a standardized particle size between 5 and 20 μ m. The surface of the AC@BKP electrodes is homogeneous, with particles always close to ~5 μ m. In **Figure 3 (b)**, we see MWCNTs entangled on the AC and with each other, as expected from a self-supported electrode of this type. In **Figure 3 (c & d)** we note that T-Nb₂O₅ has particles of ~3 μ m; MWCNTs are also entangled over the T-Nb₂O₅ particles on the BKP@T-Nb₂O₅ electrode.

Figure 3. SEM of (a-b) AC@BKP and (c-d) T-Nb₂O₅@BKP.

Figure 4 presents the *ex-situ* Raman spectrum of the T-Nb₂O₅@BKP electrode. One may observe that T-Nb₂O₅@BKP Raman spectrum (iii) combines T-Nb₂O₅ and MWCNT Raman signature. Regarding the MWCNTs used, as detailed in the literature [126–128], there is a simultaneous resonance effect on the graphene K-point, related to the π electrons and the material's phonons (double resonance). This interaction originates the D and D' bands when point or edge defects occur in nanographites; and the G' (2D) band, which does not require defects for its emergence and are related with the stacking of the graphene layers, that here is affected by the characteristic multiple-wall CNT structure [126–128]. The G band corresponds to the structural vibration mode described in the literature as E_{2g}. This vibration mode takes place at the intersection between the optical (in-plane longitudinal optical) iLO and (in-plane transverse optical) iTO phonon branches, specifically at the Γ point [126–128].

As in the case of graphene, the vibrational structure of $T-Nb_2O_5$ can be investigated based on traditional methods of solid-state physics (i.e., group theory). However, the crystal structure of $T-Nb_2O_5$ is complex. The Nb atoms are in an arrangement with six or seven oxygen atoms forming tilted octahedral (NbO₆) or tilted pentagonal bipyramidal (NbO₇) structures that together constitute an orthorhombic structure [158]. Thus, in the *ex-situ* Raman spectrum (**Figure 4**), three bands stand out, a band at ~135 cm⁻¹, one at 230 cm⁻¹, and a band at ~690 cm⁻¹, as proposed by [22].

Figure 4. Fist order Raman spectra from (i) MWCNTs buckypaper, Raman spectra from (ii) T-Nb₂O₅ powder, and (iii) T-Nb₂O₅@BKP electrode.

As already discussed by Vicentini *et al.* [50], although Raman spectrum identifies chemical bonds of the Nb₂O₅, there is a lack of information regarding the Nb-O Raman vibrations modes assign for the crystalline phase of Nb₂O₅. This approach is a challenging task because the 3D point group D2h (molecular symmetry of the T-Nb₂O₅ unit cell) theoretically has at least 84 Raman active modes [22]. Nevertheless, if one could change this structure in a specific and reversible boundary condition, it would become possible to associate these data.

Figure 5. XRD diffraction pattern from T-Nb₂O₅ powder

The XRD pattern of T-Nb₂O₅ powder materials evidenced two different polymorphic crystalline phases of niobium pentoxide, which we identified as monoclinic phase of spatial group P2 (PDF# 00-016-0053) and orthorhombic phase of spatial group Pbam (PDF# 00-030-0873). These two phases are denoted as known as TT-Nb₂O₅ with interplanar spaces 0.37 nm and T-Nb₂O₅ with 0.39 nm.

3.2 Electrochemical characterization studies

3.2.1 Electrochemical studies of the individual electrochemical contribution

Figure 6. Three electrodes individual analyses of T-Nb₂O₅@BKP (**a** & **c**) and AC@BKP (**b** & **d**). The electrochemical technique used was CV at scan-rate of 10 mV s⁻¹ (**a** & **b**) and CA at step potential of 1.2V vs. Ag. (**c** & **d**). The analyzed I vs. $t^{-1/2}$ and Q vs. t reveal each electrode's different charge accumulation mechanisms.

As shown in **Figure 6 (a)**, the T-Nb₂O₅ shows a typical voltammetric shape previously reported in the literature for Li⁺ intercalation into T-Nb₂O₅ [150,159–161]. In **Figure 6 (b)**, a rectangular-shaped EDLC cyclic voltammetry is shown. **Figure 6 (c & d)** shows *ionic diffusion* and *porous behavior* in pseudocapacitors and EDLC, respectively. The diffusion behaves like Cottrell's model ($I_{dif} \propto 1/t^{1/2}$), implying linearity in *I vs. t*^{-1/2} plot. On the contrary, a purely EDLC process (*RC* porous model) is characterized by one or two slopes in *Q vs. t* plot. In this sense, the linear T-Nb₂O₅@BKP charge behavior in **Figure 6 (c)** indicates intercalation as presented elsewhere [7,162].

Regarding the *pore accessibility* governed by the *pore resistance* (R_{in} and R_{out}), it can be evaluated from the general electrostatic model considering the $R_{ESR}-C_{EDL}$ circuit model (as

proposed in Chapter 2 of this thesis). As $I = I_0 \exp(-t/\tau)$ in a capacitor, for the R_{in} and R_{out} pores model, it follows that:

$$I_{total} = I_{0(in)} \exp(-t / \tau_{in}) + I_{0(out)} \exp(-t / \tau_{out}) + I_{res}$$
(5)

In this sense, we have the *total charge* (Q_{total}) stored at the electrode/solution interface in the presence of pore resistance is given as follows:

$$Q_{total} = \int_{0}^{t} I_{total} dt = I_{0(in)} \int_{0}^{t} \exp(-t / \tau_{in}) dt + I_{0(out)} \int_{0}^{t} \exp(-t / \tau_{out}) dt + \int_{0}^{t} I_{res} dt$$
(6)

Thus, the transient behavior of the asymptotic charge accumulation at the electrode/solution interface affected by pore resistance is:

$$Q_{total} = I_{0(in)} \tau_{in} [1 - \exp(-t/\tau_{in})] + I_{0(out)} \tau_{out} [1 - \exp(-t/\tau_{out})] + Q_{res}$$
(7)

Therefore, **Figure 6 (d)** indicates a porous behavior with two *RC* time constants $\tau_{in} = R_{in}C_{in}$ and $\tau_{out} = R_{out}C_{out}$, now demonstrated for activated carbon (AC). The relation between C_{in} and C_{out} , morphological factor, as proposed by da Silva et al. [136] shows a predominance of external pores (meso- and macro-pores). **Figure 6 (d)** shows excellent contrast in experimental and simulations ($X^2 = 10^{-9}$) data.

3.2.2 Symmetric and asymmetric configurations

Figures 7 & 8 presents the electrochemical studies performed in an asymmetric ans symmetric two-electrode setup filled with 1M LiTFSI in acetonitrile. The ion/solvent and ion/pore interaction play an essential role in the electrochemical device's specific capacitance, which implies that there should be compatibility between the electrode/electrolyte materials choice [163]. For high-voltage systems, acetonitrile-based electrolytes are often applied due to their low viscosity [164], high dielectric constant [165] and conductivity [166] that reduces the cell equivalent series resistance [167,168], increasing the device performance.

In commercial EDLCs, this organic material solvated conducting salts such TEABF₄ that quickly dissociates, increasing the ionic mobility at the electrolyte. However, in hybrid systems with battery-type electrodes, lithium-based salts are more suitable due to their cation/anion small radii size, high mobility and dissociation properties [169] contributes to the intercalation process. In this light, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) has drawn attention [170–173] due it high conductivity and thermodynamically stability that improve safety concerns. This salt thermal stability is majorly controlled by solvent reactions and could be improved by the proper solvent interaction [174]. So, in this study, we choose

1.0M of LiTFSI:ACN that presents an excellent electrochemical performance well established in literature [175–178].

Figure 7. Electrochemical studies of symmetric AC@BKP with 1M LiTFSI in acetonitrile. The best WVW determined with (a) CV (scan-rate = 10 mV s⁻¹), (b) CA techniques and (e & f) EIS. (c) CV at different scan-rates from 5 to 100 mV s⁻¹ between 2.5V-1.25V and (d) the dependence of the currents with scan rate, linear behavior (*b*-value of 1) indicates capacitive response (surface-controlled).

Figure 7 analysis helps us to identify the cell's proper working voltage window (WVW) following a method reported by our research group elsewhere [55]. Shortly, we contrast CV, CA, and EIS data and observe when capacitor behavior runs out of reality, *i.e.*, in an inappropriate WVW. At specific cell voltage, the electrolyte decomposes, wasting energy and causing gas evolution, consequently leading to cell failure. The *b*-value in **Figure 7** (d) indicates (qualitatively) the charge storage mechanism in the symmetric AC@BKP electrochemical system. The analysis of the *b*-value was posed by Lindstrom et al. [179]:

$$i(\upsilon) = a(\upsilon)^{\flat}, \tag{8}$$

where v are the scan-rate and a and b are adjustable values.

A *b*-value between 0.5 and 1 indicates an anomalous diffusion, neither surfacecontrolled (capacitive) nor diffusion-controlled (battery behavior).

Figure 8. Electrochemical studies of asymmetric T-Nb₂O₅@BKP pseudocapacitor with 1M LiTFSI in acetonitrile. The best WVW determined with (a) CV (scan-rate = 10 mV s^{-1}) and (b) CA techniques. (c) CV at different scan-rates from 5 to 100 mV s⁻¹ between 2.5V-1.25V and (d) the dependence of the peak currents with scan rate, *b*-value between 0.5 and 1 indicates an anomalous diffusion, neither surface-controlled (capacitive) nor diffusion-controlled (battery behavior).

The **Figure 8** shows the asymmetric behavior. The **Figure 8** (a) voltammogram shape is a combined behavior of balanced charges electrodes with different stored mechanisms, *i.e.*, porous and intercalation one. For a good balance device, the amount of charge Q in each electrode should always be the same but opposite (negative or positive). Thus, according to the equation and explanations proposed by Chae and Chen[180] (applicable for capacitive or pseudocapacitive devices):

$$Q = C_P V_P = C_N V_N, \qquad (9)$$

where C_P and C_N are the capacitance (F g⁻¹) of the positive and negative electrodes and V_P and $V_N(V)$ are the voltage of each electrode.

For a super- or pseudocapacitor with pronounced *Distributed Capacitance* (please see further discussion), the voltage in each electrode will not be symmetrical, as evidenced elsewhere [180]. Thus, **Equation (9)** can elucidate the T-Nb₂O₅@BKP asymmetric PC device voltammogram shape as follow: (i) between 0V and ~1.2V there is no intercalation (see further discussion), so the *Distributed Capacitance* is low and then the cell voltage is predominantly in the T-Nb₂O₅@BKP electrode; (ii) as we go for more positive voltage, the intercalation increases the energy storage in niobium oxides; (iii) the *Q* changes remain balance, however, the speed of charge is limited by the intercalation process. Therefore, the rectangular shape EDLC behavior will act as an offset current for the T-Nb₂O₅ at constant SR, **Figure 6 (a)**. The result is the **Figure 8 (a)** for the voltammetry and an inflexion on the GCD curve, **Figure 9 (b)**.

Figure 8 (c) shows CVs within the best WVW (*i.e.*, 2.5V) at various scan rates of 5– 100 mV s⁻¹. Initially, the electrode was cycled to perform electrochemical stabilization. To determine the best *working voltage window* (WVW) of the asymmetric T-Nb₂O₅@BKP PC, the method proposed by our group elsewhere was employed [181]. Firstly, CV measurements in **Figure 8 (a)** were conducted at 10 mV s⁻¹ in different voltages as 2.3, 2.4, 2.5 and 2.6V. In the changing process from voltages higher than 2.5V, there is an increase in the current response, indicating maybe electrolyte decomposition. **Figure 8 (b)** shows the CA technique to different voltages. In this *single-step voltage* (SSV) experiment, an exponential decay is expected to capacitive interfaces and is represented by equation $I = I_0 \times \exp(-t/\tau)$, where τ is the s time constant ($\tau = RC$). For capacitive interfaces, the current after a long period must tend to zero (*i.e.*, $I/I_0 \le 0.001$) [7,55]. The inset graph in **Figure 8 (b)** shows the ratio for I/I_0 for the T-Nb₂O₅@BKP PC after t = 120 s. The increase in the residual current ratio reached values suitable for a supercapacitor up to 2.5V, *i.e.*, $I/I_0 \le 0.001$. The variations of this behavior for organic electrolytes are related to solvent decomposition. Thus, 2.5V was the best WVW of the asymmetric T-Nb₂O₅@BKP PC. The charge storage process involving it intercalation reaction in the T-Nb₂O₅ can be represented as [139]:

$$Nb_2O_5 + xLi^+ + xe^- \leftrightarrow Li_xNb_2O_5$$
(10)

where $x \leq 2$.

In practice, according to Chen et al. [161] the x value is about 1.1 (about 8.8 Li+ per unit cell).

The CVs took from 5 to 100 mV s⁻¹ presented in **Figure 8 (c)** and data of the peak current fitted in **Figure 8 (d)** reveals the non-linear region among 5 to 100 mV s⁻¹ for the peak currents, representing the capacity limited by an anomalous diffusion of the AC@T-Nb₂O₅ PC, *i.e.*, a hybrid battery and supercapacitor behavior.

Figure 8 (e & f) shows the EIS data in 2.5V to confirm the best WVW in the frequency domain. A well-behaved SC without parasitic reactions must have a vertical line with a phase angle close to 90° [7]. However, the asymmetric T-Nb₂O₅@BKP PC has the negative electrode formed by T-Nb₂O₅ which inserts faradaic reactions to the system, considerably reducing the phase angle (*i.e.*, \sim 70°).

The *Gravimetric Charge Discharge* tests were performed with different gravimetric currents varying from 0.1 to 2 A g⁻¹, presented in **Figure 9 (a & b)** for both devices. The triangular shapes typically from EDLCs are observed in GCD curves of AC@BKP SC devices (**Figure 9(a)**). A *quasi-plateau-like* shape is observed in **Figure 9 (b)**, but they do not have constant cell voltage as in batteries. **Figure 9 (c)** contrasts GCD curves.

Figure 9 (d) shows the "*Distributed Capacitance*" extracted from GCD data as a function of normalized discharging time (t/t_{max}). The latter contrasts both devices at 0.1 A g⁻¹. In the range analyzed for the symmetric AC@BKP devices, we see a straight line, a nearly constant distributed capacitance, *i.e.*, there is enough time for proper organization of the ionic species even into the smaller pores with high time constants ($\tau = RC$). We can also conclude that different gravimetric currents (higher or lower) allow us to infer the time of each reaction in the device.

Therefore, for **Figure 9 (d)** regarding the T-Nb₂O₅@BKP PC device, as the capacitance of the EDLC electrode is constant at this current, the variation between 30 and 20 F g⁻¹ characterizes the behavior of the T-Nb₂O₅ electrode. The **Figure 9 (c & d)** also shows a GCD and *Distributed Capacitance* for the WVW of 2.3V. This result is significant because it shows a *Distributed Capacitance* more like an AC supercapacitor behavior (linear) for a different state of charge (SoC), i.e., less charge (SoC smaller) is seen to be faster.

Figure 9. Galvanostatic discharge curves at WVW with different densities currents for the (a) symmetric and (b) asymmetric device, (c) GCD comparison at 0.1 A g^{-1} and (d) the distributed capacitance obtained from the GCD data at 0.1 A g^{-1} . (e) Cycling stability and retention. (f) Ragone plot of the specific energy (E) and averaged specific power (P_{med}) for both devices.

The Ragone plot in **Figure 9 (e)** compares the AC@BKP SC and the T-Nb₂O₅@BKP PC devices. The specific energy (E) of the AC@BKP SC and T-Nb₂O₅@BKP PC at 0.1 A g⁻¹

are 6.5 and 16 Wh kg⁻¹, respectively. At 1 g⁻¹, *i.e.*, in a discharge of approximately 20 seconds for the PC, the results are 5.6 and 10.7 Wh kg⁻¹. The T-Nb₂O₅@BKP PC device has almost twice the energy of the AC-based symmetric supercapacitor. The specific averaged power at 2 A g⁻¹ (~5 seconds discharge time) was ~3.6 kW kg⁻¹ for both devices. Even in the latter case, the PC energy was ~45% higher. They exhibit excellent energy storage properties with simultaneous high specific energy (compared with the AC-based) and good specific power. With these lines, it is reasonable to conclude that optimized asymmetric T-Nb₂O₅@BKP pseudocapacitors could be one promising energy storage device to replace battery technologies such as Lead–acid batteries regarding specific energy & power characteristics. Environmental concerns must be examined in detail, as Lead-acid technology can be recycled. It is worth mentioning that the intercalation tends to cause stress on the network, affecting the aging aspects of the device, and that could be tested by cycling the devices several thousand times, which is underway in our group.

3.3 Raman operando studies

To further assess the electrochemical behavior and structural changes during the device's charging & discharging cycles, Raman *operando* studies were employed in the T-Nb₂O₅@BKP negative electrodes using 2 electrodes configuration. **Figure 10** shows the Raman *operando* spectra taken during a CV at 1 mV s⁻¹ within 2.5V of WVW. There is a substantial increase in the current responses in the voltages higher than 1.25V of the charging process, and the same trend is observed in the discharging process. A decrease in the current can be seen in voltages lower than 1.25V. Such increase and decrease are related to the Li⁺ intercalation that was calculated to occur in the (001) T-Nb₂O₅ plane owing to the low-energy diffusion barrier (caused by a large oxygen–oxygen distance, 3.9 Å) between adjacent NbO₆ octahedra [22].

Figure 10. Operando Raman spectra of T-Nb₂O₅@BKP PC. (a & b) Evolution of Raman spectra of a charge and discharge cycle at 1 mV s⁻¹ in the WVW of 2.5V. Colored frame in right corner shows the applied voltage of each spectrum. (c) The intensity (in Counts) color mapping image showing 3 voltametric cycles.

Figures 10 (a) and **(b)** present the spectra during the charge and discharge, respectively. Here, the frame in the right corner exhibits the applied voltage for each Raman spectrum (*i.e.*, 0-2.5V). The whole spectra can be divided into two regions: (*i*) Carbon region from 1100 to 1700 cm⁻¹ which are represented by G-, D-, and D'-bands (typical first-order Raman spectra of nanographites). The G-band is related to E_{2g} Raman active phonons at the Brillouin zone, and the D- and D'- bands are point or edge defects-induced; (*ii*) T-Nb₂O₅ region from 100 to 1000 cm⁻¹ that were assigned to the v_{Hi} and v_{Mid} . v_{Hi} occurs at 500-700 cm⁻¹. The bands verified at 629 and 679 cm⁻¹ are assigned by Huang et al. [182] as an transverse optic modes. In the case of v_{Mid} , it occurs at 100-350 cm⁻¹. The band at 178 cm^{-1 1} was assigned by McConnell et al. [183] to external modes, while that at 279 cm⁻¹ was assigned to the triply degenerated vibration mode in the T_{3u} region [50,183].

From the discharge spectra in **Figure 10** (a), it is possible to verify that from voltages between 0 to 1.25V the whole spectra remain static, with no or slight variations. On the other hand, from higher voltages between 1.5 to 2.5V the carbon region almost disappears. Besides, there is a substantial decrease in the intensity of the v_{Hi} and v_{Mid} regions. In the discharge process in **Figure 10** (b), the same trend is observed but inverted. Such behavior may indicate a double layer formation over the MWCNT tangle on the T-Nb₂O₅ particles and can be related to the Tyndall effect [184]. As this chapter presents in **Figure 1** (c & d), the superficial MWCNT layer over the T-Nb₂O₅ is thin. Therefore, although the MWCNT is very sensitive to infrared, voltages such as 2.2V proved to suppress these characteristic bands of the MWCNTs spectra.

Considering the V_{Mid} intensity band changes during the charge & discharge Li⁺ intercalation in the T-Nb₂O₅@BKP electrode, this band can be assigned to exclusively cornersharing along [001] (plane c) Nb-O stretching mode, as reported by [22] and by Nb-O edge defective vibrations. One *ex-situ* previously reported work shows the Nb₂O₅ phase Raman spectra with different annealed temperatures (high temperatures are related to the crystalline phases). This method reveals an arising of well-defined bands between 100 and 350 cm⁻¹ compared to the amorphous Nb₂O₅, so assigned to crystallinity (monoclinic or orthorhombic) [185]. Thus, the V_{Mid} may be related to monoclinic or orthorhombic edge crystal defects, mainly affected by the T-Nb₂O₅ unit cell a-axis and c-axis expansion and decreases of b-axis values during the lithiation process.

To our knowledge, the above finds are intrinsic to the charge storage process between Li^+ and T-Nb₂O₅ and confirm previous literature works [22]. In a nutshell, our data shows that


the Li⁺ intercalation in the T-Nb₂O₅ during the asymmetric device charge & discharge process causes changes in the intensity of v_{Hi} and v_{Mid} bands.

Figure 11. T-Nb₂O₅ unit cell from different perspectives, made in the (VESTA) software [186]. Adapted from [22,149].

These intensities decrease can be further accessed by **Figure 10** (c), in which a twodimensional image presents the Raman intensity varies according to the applied voltage. Here, the reversible behavior is confirmed by three cycles of CV. On the left side of **Figure 10** (c), a color bar mapping the intensities (in Counts, not normalized) variation is shown. As a periodic behavior, when 0.0V is applied at the beginning of the charging process, all bands have their maximum intensity. However, even after intercalation, it is still possible to perceive a pattern in the bands between 100 and 350 cm⁻¹, but it is weak and close to an amorphous Nb₂O₅. This matches with: *(i)* a disturbance in the structure that facilitates interaction, an increase of interplanar distance c-axis, for instance; and *(ii)* that something *changes the perception* of the material's crystallinity by Raman spectroscopy, as adsorbed ions in the bulk surface material modifying the Nb-O edge vibrations.

4. Conclusion

In this investigation, the aim was to assess the niobium oxide (Nb₂O₅) and multi-walled carbon nanotubes (MWCNTs) electrochemical energy storage behavior. We explored it as an electrode material for Li-ion hybrid pseudocapacitors (PC) in asymmetric configuration with a buckypaper-type (BKP) active carbon (AC) electrode. Considering the discharge of ~20 seconds (1 A g⁻¹) the T-Nb₂O₅@BKP asymmetric pseudocapacitor showed almost twice the energy of the AC-based symmetric supercapacitor under the same conditions. The interaction between Faradaic and non-Faradaic processes needs to consider the time constants involved in each process. In this sense, the *distributed capacitance* applied to pseudocapacitance devices has proven to be a good way to evaluate this complex interaction. The average capacitance of the T-Nb₂O₅@BKP asymmetric pseudocapacitor was ~25 F g⁻¹ at 0.1 A g⁻¹ and ~12.5 F g⁻¹ for the AC-based symmetric supercapacitor devices. Operando Raman spectroscopy was applied to help understand the energy storage mechanism, evaluating the structural changes while recording the charge and discharge curves. Regarding the asymmetric one, energy and power densities of 16 Wh kg⁻¹ and ~3.6 kW kg⁻¹, respectively, arising from the combination of the characteristics of MWCNTs (large voltage window and chemical stability), AC (high surface area), and T-Nb₂O₅ (facilitated intercalation of Li, additional pseudocapacitive properties) were achieved. Ultimately, we propose a high power density pseudocapacitor with high stability and more energy than a conventional AC-based supercapacitor. This way, we hope to have contributed to the electrochemistry of hybrid devices.

Chapter 4 General conclusions

The present study confirms the hypothesis that high surface area carbon electrodes can improve the electrical characteristics of supercapacitors. Especially MWCNTs, with high power densities and excellent electrical properties, have been proved a great *scaffold*. Thus, it was used with AC and T-Nb₂O₅ in Chapter 3 as an MWCNTs buckypaper electrode.

The oxygen plasma functionalization of the MWCNTs as a buckypaper electrode shows that: (i) plasma treatment exfoliated MWCNT increasing defective areas at the external interface and bringing them together by electrostatic forces, forming mountain and valley structures in the buckypaper top surface; (ii) surface oxygenated functional groups increased from ca. 2 to 30% after the plasma treatment; (iii) the overall charge-storage characteristics of the symmetric supercapacitor device increased by *ca*. 10% after the plasma treatment.

Although a higher increase in energy storage was initially expected, the MWCNTs *per se* suffer from low energy density because their inner multiples walls are not electrically active. Further, in an aqueous medium, the best *Working Voltage Window* (WVW) was 1V for both device studies, as-prepared and functionalized MWCNTs.

However, the study of these devices with plasma-induced surface changes allowed a theoretical model proposed to represent distributed capacitance behavior affected by the electrolyte resistance inside the different porous structures.

A central question arose regarding combining a battery-type electrode and an essentially supercapacitive (non-Faradaic) electrode: *is this device a low capacity battery or a reliable pseudocapacitor with more energy*?

As discussed in chapter 3, a single electrochemical device can't exhibit at the same time high specific energy and power values since the magnification of one parameter demands suppression of the other, *i.e.*, the time-scale of the physicochemical events inherent to SCs and batteries are linked to different phenomena occurring at the electrode/solution interface and in the bulky region of the electrode material, respectively.

However, this combination was done using an intercalation pseudocapacitance type (T-Nb₂O₅) electrode and an EDLC type (AC) in an asymmetric device configuration. The interaction between Faradaic and non-Faradaic processes, capacitance and capacity, needs to consider the time constants involved in each process. In this sense, the *distributed capacitance* applied to pseudocapacitance devices and electrodes has been proved an excellent way to evaluate this complex interaction. The T-Nb₂O₅ allows a fast Faradaic reaction of lithium-ion diffusion throughout the bulk of the active material. In this sense, the *operando* Raman analysis was crucial for clarifying the electrochemical mechanisms of the material and its surface, as well as the Li⁺ intercalation potentials at two electrodes configuration.

An in-depth study of EIS can be performed in future works, as well as an electrochemical analysis of both electrodes, working and counter electrodes, simultaneously, to

clarify aspects related to the ideal mass ratio in hybrid pseudocapacitors. Furthermore, longterm cyclability and the environmental context are also important issues.

Therefore, is the T-Nb₂O₅ Faradaic intercalation reaction fast enough? It is enough for a high-power energy storage device, a pseudocapacitor device. It stores 45% and ~2.5 times more energy than an AC-based supercapacitor, considering charge-discharge times between 5 seconds and 2 minutes, respectively, in the same conditions and with similar power capabilities.

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