

Carbon materials for an efficient use of energy by electrochemical devices

Materiales de carbono para un uso eficiente de la energía en dispositivos electroquímicos

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Abstract

The efficient use of energy, in particular electricity, requires devices allowing its storage and subsequent conversion into work with a high yield. Electrochemical devices are very effective since the absence of mechanical moving parts reduces irreversibility and provides high efficient conversions. The efficiency of the device depends on the performance of the electrodes, which depends on the properties of the materials that compose them. Because most of the electrodes are made from carbons, this field of research has experienced a tremendous growth in recent years, in particular for three devices: Proton Exchange Membrane Fuel Cells, Lithium Ion Batteries and Supercapacitors. This article presents the latest research trends in this field taking as a reference the papers presented at the Carbon 2012 Conference recently held in Krakow.

Resumen

El uso eficiente de la energía, en particular de la energía eléctrica, requiere de dispositivos que permitan su almacenamiento y posterior conversión en trabajo con alto rendimiento. Los dispositivos electroquímicos son especialmente eficientes ya que la ausencia de elementos mecánicos móviles permite conversiones con una eficiencia muy elevada. El rendimiento global del dispositivo depende de las prestaciones de los electrodos, las cuales dependen de las propiedades de los materiales que los componen. La mayor parte de los electrodos están elaborados con materiales de carbono, por lo que este campo de investigación ha experimentado un enorme crecimiento en los últimos años, en particular los relacionados con Pilas de Combustible Poliméricas, Baterías de ión litio, y Supercondensadores. En este artículo, se presentan las últimas tendencias en investigación en estos dispositivos tomando como referencia los artículos presentados en la pasada Conferencia Carbon 2012 celebrada en Cracovia.

1. Introduction

Electrochemical devices are very effective for the efficient use of energy, in particular electricity, allowing its storage and subsequent conversion into work with a high yield since the absence of mechanical moving parts reduces irreversibility and provides high efficient conversions. The efficiency of the device depends on the performance of the electrodes, which, in turn, depends on the properties of the materials that compose them. Because most of the electrodes currently used for energy purposes are made from carbons, this field of research has experienced a tremendous growth in recent years, in particular for three devices: Proton Exchange Membrane Fuel Cells, PEMFC, Lithium Ion Batteries, LIB and Supercapacitors, SC. Figure 1 shows the energy and power density of the three types of devices considered. Comparing SC (Electrochemical

capacitors) with LIB, the formers show higher power density, shorter response time (1-30 s for SC vs 0.5-1 h for LIB) and longer cycle life (up to 1,000,000 cycles for SC vs up to 1,000 cycles for LIB). In contrast, SC show lower energy densities. PEMFC shows the higher energy density since this is only limited by the fuel storage capacity.

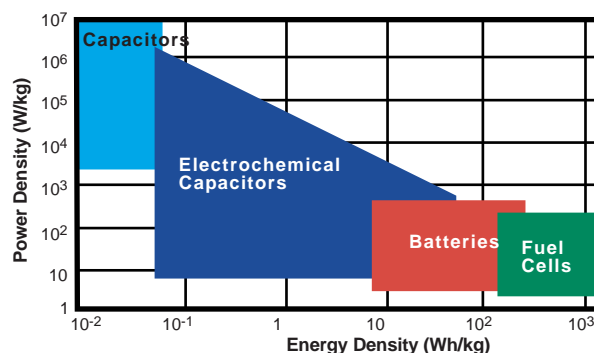


Figure 1. Energy and Power density of different electrochemical devices.

Figura 1. Energía y densidad de potencia de diferentes dispositivos electroquímicos.

2. Proton Exchange Membrane Fuel Cells, PEMFCs

H₂/air fuel cells based on proton-exchange membranes have many attractive features which make them a promising clean energy technology for powering hybrid Electric/FC vehicles. In portable applications, using direct alcohols DAFC, including bio-alcohols, is an option that is pushing the access to the market of this type of FCs. Despite the many advances made in PEMFC development, improving their performance, in particular the electrocatalyst, is still needed. In particular, reducing intolerance to CO, increasing the Oxygen Reduction Reaction kinetics and reducing cost. Efforts are being focused to reduce Pt content by alloying with cheaper metals and substituting the carbon supports by novel ones with improved performances.

CoOx-MWNTs nanocomposite as a support for Pt nanoparticles has been proposed as potential promoter for methanol electro-oxidation reaction. The results of electrochemical tests showed that the CoOx improved Pt/MWNTs performance in terms of activity and stability [1]. Non-metal Carbon alloy catalysts which acquire the catalytic activities by introducing heteroatoms, different types of chemical bonding or unique morphologies to the original carbon structures have been proposed. A catalyst prepared by ammoxidation (AO) treatment of carbon nano-onions which were obtained by heat-treatment of a nanodiamond has been reported [2]. Tungsten carbides and tungsten nitrides have been proposed to substitute Pt. These materials show a very low catalytic effect for the Oxygen Reduction Reaction, but the addition of a small amount of platinum in the tungsten hemicarbide surface enhances the catalytic effect [3]. Pd based catalysts coated on MWCNTs

synthesized with Au as second metal and CeO_2 addition to prevent CO poisoning have also been reported. This type of catalyst is specially indicated for new renewable energy using direct formic acid in fuel cells [4].

Improving the performance of the support is a key to improve the catalyst activity allowing reducing the Pt content. The electrocatalyst supports should have a high surface area, electronic conductivity, a suitable pore structure and surface chemistry. Carbon blacks, in particular Vulcan XC-72® are currently used as support for electrocatalyst because they fit these properties at low cost. To improve these performances, novel carbon materials have been proposed: Carbon xerogels have been reported as catalyst supports for FC applications. The specific catalytic activity significantly increases when Vulcan is substituted by mesoporous xerogel carbons in passive DMFC configuration [5]. Pt and Pt/Ru nanoparticles supported on carbon nanofibers, CNF's have been tested and higher catalytic activity than using Vulcan has been reported. The CNF properties have shown to influence the Pt dispersion and distribution [6]. Carbon nanocoils (CNC) have recently received great attention due to the combination of their good electrical conductivity and a wide porosity. The behaviour of a Pt/CNC catalyst on the anode side of a PEM fuel cell was compared with the commercial E-TEK Pt-supported catalyst. Results showed better performance for the CNC-supported electrocatalysts [7].

Superiority of MWCNT and graphenes as catalyst support has been reported with the only drawback of high cost of these materials. Graphite Nanofibres, GNF, have been proposed as substitute for MWCNT and also as a low cost graphite source for graphene production [8]. Catalytic activity of Pt clusters can be promoted by using the interface interaction between Pt and CNT surface [9]. It has been found that graphenes and carbon nanotubes (CNTs) can act as effective metal-free electrocatalysts [10]. Improved electrocatalytic activity is due to the net of positive charged carbon atoms created in graphene site or nanotube wall. Several strategies are used to obtain graphene/CNT positively charged carbon nets. Functionalization of CNT causes enhanced electrocatalytic performance. Another approach is to put the graphene or nanotubes in highly electrophilic polymer matrix. The third way is incorporation of donor atoms into graphene/CNT site during growth. Growth of the CNTs on Si/SiO_2 by using spray pyrolysis CVD technique has been reported. Heteroatom doped carbons are receiving particular attention due to their superior performance in the ORR. N-doping is an essential factor for the catalytic efficiency of carbon-based catalysts and sulphur is receiving increasing attention as a dopant.

3. Ion Lithium Batteries, LIB

A Lithium Ion Battery is a device that stores electricity as chemical energy and then converts back this energy into electricity. Figure 2 shows the main components. There are two electrodes and an electrolyte that allows the transfer of ions between them. The interest for a LIB is the use as electrodes of materials capable of inserting Li ions, in a reversible manner, within its structure. The commercial LIB use metal oxides containing Li as cathode and different graphitic materials as anodes. Efforts in LIB development are focused in finding cheaper and sustainable graphite sources and increasing the Li intercalation capacity of electrodes.

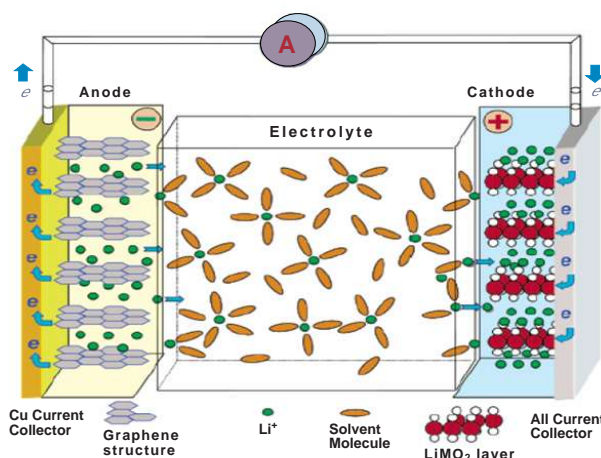


Figure 2. Main components of a Li-ion battery.

Figura 2. Principales componentes de una batería ion-Li.

3.1 Advanced 3D cathodes based on Metallic Oxides/Carbon composites

A new approach, previously used for supercapacitors, consisting of carbon nanotubes (CNTs) and conducting polymers (ECPs) with high specific power, high specific energy, and stable cycling performance through a 3D design, has been adapted to improve the power density of LIB and make it comparable with that of supercapacitors. New nanostructured cathodes based on MnO_2 , supported on MWCNT have been reported [12]. The as-synthesized materials show a capacity up to $134 \text{ mAh}\cdot\text{g}^{-1}$ after 100 cycles discharge and charge at $150 \text{ mA}\cdot\text{g}^{-1}$.

Olivine-type LiFePO_4 is receiving attention as cathode material due to its high theoretical specific capacity ($170 \text{ mAh}\cdot\text{g}^{-1}$), thermal stability, safety, and potentially low cost. However, the inherent poor electronic conductivity and Li-ion diffusion coefficient at room temperature bring difficulties for high-rate battery applications. Modifications of LiFePO_4 particles by minimizing the particle size and coating them with an electron-conducting carbon layer are considered to be effective in surmounting electronic and ionic transport limitations. A Ethylene glycol (EG)-mediated solvothermal route for the large-scale synthesis of nest-like LiFePO_4 hierarchical microstructures constructed from nanoplates by using Li_2SO_4 , $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ and P_2O_5 as raw materials, [13]. After 100 cycles, a stable capacity of $158 \text{ mAh}\cdot\text{g}^{-1}$ is obtained, indicating a good electrochemical reversibility and structural stability of the material.

3.2 Anodes based on synthetic graphite and decorated nanocarbons

Natural and synthetic graphite have been extensively investigated searching for an ideal anode material in terms of capacity, cyclability, operational voltage and cost. Crystalline graphite can insert up to one Li ion for every six carbons to form the intercalation compound LiC_6 what corresponds to a theoretical reversible capacity of $372 \text{ mAh}\cdot\text{g}^{-1}$. Currently, petroleum coke is used as the main precursor material in the manufacturing of synthetic graphite. However, different factors concerning cost and sustainability have prompted a research interest into other alternative precursors. Carbon Nanofibers (CNFs) obtained from natural gas and biogas have been proved to be an excellent graphite source due to their significant degree of structural order that can be significantly improved by catalytic treatment with Si at high temperature [14]. Efforts are devoted to incorporate materials with higher Li intercalation

capacity than graphite. SnO_2 and Si are the most extensively studied due to their significant higher Li capacity (781 mAhg^{-1} for SnO_2 and 3580 mAhg^{-1} for Si) low cost and low toxicity. The main drawback for their use in a real application is the low reversible capacity retention due to substantial changes in volume during the alloying/dealloying process (the so called "pulverization" problem). One of the promising methods to overcome this is to prepare Si/carbon nanocomposites by covering Si nanoparticles with carbon nanolayers by CVD. The structure of carbon-coated Si nanoparticles (nano-Si/C) is drastically changed during charge/discharge cycles in the early cycles and becomes a dendrite-like structure where Si and carbon are uniformly mixed. The dendrite-like structure has been retained over 100 cycles and nano-Si/C exhibited excellent performance (1500 mAh.g^{-1} at 3.3C) and good cyclability (1500 mAh/g) [15].

A very effective strategy for buffering variations in volume is the use of nanoparticles of Si and SnO_2 deposited in a carbonaceous matrix, whose structure confers mechanical stability. Several carbonaceous matrixes have been used. Thanks to their amorphous structure and their individualized nanosized morphology, the Si nanoparticles deposited by Fluidized Bed CVD on the CNTs are able to be loaded with Li with excellent specific capacity on the very first charge-discharge cycles [16]. However, degradation of the electrode has been observed. This led to an irreversible capacity, added to the first discharge reversible capacity (total of 3187 mAh/g). A mean capacity loss of 2 % per cycle is observed from the 2nd to 26th cycle.

Concerning SnO_2 composites, they show a lower initial capacity but a higher cyclability. SnO_2 -carbon composites made up of tin oxide nanoparticles deposited onto the surface of a graphitic nanocarbon synthesized by a novel synthesis process based on the pyrolysis of Fe (II) gluconate exhibit very good electrochemical performance against lithium. Indeed, a capacity of 400 mAh/g for SnO_2 -nanocarbon was recorded after 50 cycles [17]. SnO_2 -Graphene composite [18] synthesized by deposition of SnO_2 nanocrystals onto the surface of graphene, presented a superior cycling stability up to 500 cycles with a capacity of 480 mAh g^{-1} . Such good stability could be ascribed as the strong adhesion of SnO_2 nanocrystals on the graphene support, which is of a high electronic conductivity and possesses good flexibility.

A sol-gel approach was used to synthesize LSTO/CNF anode materials by doping LTO particles with Sn^{2+} and incorporation of CNFs has been reported. The LSTO/CNF composite electrodes delivered a remarkable capacity of 122 mAh g^{-1} after charging/discharging at 10C for 500 cycles [19]. Graphene Nanosheet Aggregations, GNSA, analyzed under various current densities of 50 mA/g shown a first discharge and reversible charge capacities of 1647 mA h/g and 528 mA h/g respectively. And the reversible ischarge capacity remained at ca. 411 mAh/g after 50 cycles (0.5% capacity fading per cycle at 50 mA/g) [20].

4. Supercapacitors

Supercapacitors (SCs) can deliver higher power in a shorter time than batteries. However, for their use in certain applications it is first necessary to increase their energy density. Among the electrode materials used in SCs, carbons have been the most developed due to their excellent properties. Energy is stored in

a supercapacitor by two mechanisms: (i) double-layer mechanism, which consist in an accumulation of the electrolyte ions at the electrolyte/electrode interface, and (ii) pseudocapacitive mechanism, in which oxidation/reduction of the electrode is accompanied by extraction/insertion of electrolyte ions. The former mechanism works in the so called Electric Double Layer Capacitors, EDLC's. The latter has been found in transition metal oxides, and also in carbons having a high content in oxygen and/or nitrogen groups (i.e. highly functionalized carbons). Figure 3 shows the main components of both types of SC.

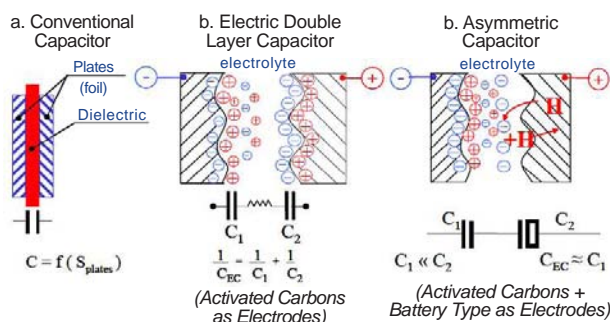


Figure 3. Main components of the different types of supercapacitors.

Figura 3. Principales componentes de los distintos tipos de supercondensadores.

Increasing energy density of carbon-based SCs (CBSCs) has been centred in two approaches: (i) Developing size-controlled porosity for EDLC's and (ii) Enhancement of capacitance through pseudocapacitive contributions provided by functional groups from physical/chemical treatments, by polymers deposition or by the insertion of transition metal oxide particles.

4.1. Carbons for Electric Double Layer Supercapacitors, EDLC's

EDLC's store energy in a polarized double layer at the interface between an ionically conducting electrolyte solution and an electronically conducting electrode. Currently efforts focus on improving the energy density of EDLC's by tuning the pore size of micro-porous carbons to increase the capacitance. The pore size leading to the maximum double layer capacitance is very close to the desolvated ion size, and the major electro-adsorption process takes place around 0.7 nm in aqueous media and 0.8 nm in organic electrolytes. Cyclic activation of non porous carbons by H_2O_2 , at 89 bars and $200 \text{ }^\circ\text{C}$, followed by the decomposition of the surface functionalities, has shown to be an effective method for producing microporous carbons. After 4-5 treatment cycles, the specific surface area is between $1000\text{--}1200 \text{ m}^2\text{.g}^{-1}$ and the pore entrances are adapted for the use in organic based electrochemical capacitors. The pore size can be tailored to the electrolyte ions size through one cycle by adjusting the reaction parameters i.e. pressure, temperature and time [21]. Up to now it is not clear what materials (micro- or mesoporous) are more suitable. In mesoporous carbon materials with definite well-ordered pore channels, there is unhampered in-pore ionic transit, that should show the best results in the area of supercapacitor technologies. Cyclic voltammetry of mesoporous and microporous carbon samples prepared by carbonization ($600\text{--}800^\circ\text{C}$) with alkali excess showed that mesoporous carbons are more suitable candidates for SC electrodes, than the microporous ones. The origin lies in predominance

of capacitance of EDL in the case of the mesoporous samples. For the microporous samples, faradaic processes arise, which lead to slowdown of charge-discharge process and decrease in maximal number of cycles [22].

A synthesis process of carbon xerogels based on the use of microwave radiation to promote reactions between resorcinol (R) and formaldehyde (F) monomers has been reported. The carbon xerogel, AOX, was compared to commercial activated carbons and, in all the evaluated media, AOX showed a better electrochemical performance, revealing the importance of small-sized mesopores in energy storage processes. Results obtained with different asymmetric cell configuration capacitance showed values of 213 F.g⁻¹ using a maximum voltage of 1.6 V [23]. Hydrothermal carbonization has demonstrated to be an effective synthetic route for the production of functionalized carbonaceous materials from simple monosaccharides, such as glucose and xylose. The symmetric capacitors obtained from the hydrothermal treatment of the hydrolysis products of spruce and corn cobs exhibited good energy densities, with values of 6.4 and 7 W h kg⁻¹ and power densities of 0.76 and 1.08 kW kg⁻¹ in a voltage window of 0.8 V and current density of 250 mA/g, with high coulombic efficiencies [24].

4.2. Heteroatom Doped Carbons

To achieve high performance supercapacitors, the use of heteroatom-doped graphenes and MWCNT as electrode material has also been proposed. Boron- and nitrogen-doped graphene samples prepared by the combined plasma treatment and high-temperature thermal treatment have been used and a large increase in the specific capacitance was observed [25]. N-doped carbons from amino containing carbohydrates; macro-mesoporous N-doped carbogels from glucose and albumin; microporous N-doped materials from glucose and algae; non-porous dual sulphur-nitrogen-doped carbon microspheres from glucose and cysteine or thienyl-cysteine; hollow spheres doped solely with nitrogen, solely with sulfur or with both nitrogen and sulfur have been proposed [11]. The N-doping of activated carbon electrode by ammonium carbamate treatment has been shown to be effective in improving the durability against the high voltage charging for electric double layer capacitor [26]. Vanadium nitride/carbon nanotube (VN/CNTs) nanocomposites obtained by sol-gel synthesis of VN in presence of CNTs has been reported. Introduction of CNTs to obtain the VN/CNTs composites leads to a significant increase of the total surface area and pore volume. The VN nanoparticles are homogeneously dispersed and their rich-oxygenated surface is accessible for redox reactions with the electrolyte ions. The electrochemical properties of supercapacitors built with these nanocomposite electrodes are improved compared to a system built with VN or VN mechanically mixed with CNTs. Capacitances of 270 F/g of VN and 171 F/g of electrode were reported [27].

4.3. Carbon doped with Re-dox systems for Pseudo-Capacitance induced Supercapacitors

The technique called "super growth method" has been developed to mass-produce highly pure SWCNTs (hereinafter, referred to as "SG-SWCNTs") containing impurities such as metals and amorphous carbons in small amounts. The method enables to synthesize a few millimeter-long SWCNTs aligned perpendicularly on the substrate in a short time. Due

to these advantages, a SG-SWCNT capacitor cell can work at 3.5V achieving an energy density of 16 Whkg⁻¹ and a power density of 10 kWkg⁻¹. A 1400F capacitor cell has been produced [28]. The direct growth of graphene/SWCNT hybrids by CVD with FeMgAl layered double hydroxides as the catalyst precursor has also been reported. The combination of graphene and SWCNTs prevented them from aggregating and the unique structure endowed the high-rate transportation of electrolyte ions and electrons throughout the electrode matrix, which gave rise to the high electrochemical performance of the hybrids. A maximum specific capacitance of 156 F/g was obtained at a scan rate of 10 mV/s. The graphene/SWCNT electrode also showed a good cycle performance, and the capacity retains 95 % of the original value after 5000 cycles at a scan rate of 100 mV/s [29].

A low cost alternative treatment based on the introduction of redox-active molecules has been studied: The incorporation of the methylene blue-redox system to an MWCNT-based EDLC led to an increase of four and a half times the original cell capacitance value provided by MWCNTs in sulfuric acid (from 5 to 23 F.g⁻¹) with no significant increase in the ESR and an excellent long-term cycling behaviour (reduction of 12% in capacitance after 6,000 galvanostatic cycles). Capacitance values of 71 F/g and 131 F/g for anode and cathode have been reported [30]. Carbon-based electrochemical capacitors operating in different aqueous solutions with various dihydroxybenzenes as source of pseudocapacitance have been reported. The highest capacitance values (283 F g⁻¹ at 5 mV.s⁻¹) were observed for 0.38 mol.L⁻¹ hydroquinone dissolved in 1 mol.L⁻¹ H₂SO₄. Similar values were obtained for alkaline electrolyte with hydroquinone (275 F g⁻¹ at 5 mV s⁻¹) being higher than for electrolytes without dihydroxybenzenes [31].

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