# Electrochemical Applications of Carbon Materials: a recent perspective from The World Conference on Carbons 2018

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## Abstract

This article analyzes the contributions on the Electrochemical Applications Topic presented in the last World Conference on Carbon 2018. The subject and relative proportion of these contributions are proposed to be an objective indicator of worldwide current research activity in the field. Moreover, some of the new findings and trends on carbon materials for supercapacitors, batteries and fuel cells are discussed.

## Resumen

El presente artículo analiza las contribuciones sobre "Electrochemical Applications Topic" de los materiales carbonosos presentadas en el último congreso mundial World Conference on Carbon 2018. Se propone utilizar la temática y proporción relativa de estas contribuciones como un indicador objetivo de la actividad investigadora actual en este campo. Además, se discuten algunos de los nuevos avances y tendencias sobre los materiales carbonosos en supercondensadores, baterías y pilas de combustible.

## 1. Introduction

Carbon materials represent a wide, unique, and one of the most versatile families of materials, exhibiting different allotropic forms, dimensionality, morphology-conformation-dimension, crystalline structure, porous texture, and surface chemistry. All these features make carbon materials to display several extraordinary properties for multiple industrial applications and technologies. Consequently, research on the field of carbon materials generates significant interest in multidisciplinary fields.

At present, many indicators may be useful to describe the state of the art on carbon materials. For example, the number of scientists and research groups on carbon materials; markets of conventional as well as novel carbon materials; the annual number of articles and impact of journals related to carbon science, and so on. Moreover, national and international conferences may constitute exceptional thermometers of local or worldwide research activity in the field.

Since it was born in 1956, the World Conference on Carbon is an international conference of the highest authority in this field. This annual meeting, sequentially organized by the Asian, European and American Carbon Societies, gathers the rich and multidisciplinary community of scientists and technologists working on the preparation, characterization and study and application of carbon materials. Although the participation may be partly conditioned by geographical issues, the analysis of the communications presented in this meeting may provide an objective view of the state on the art on carbon materials research.

One of the exceptional properties of carbon materials is their electrical conductivity, which mainly arises

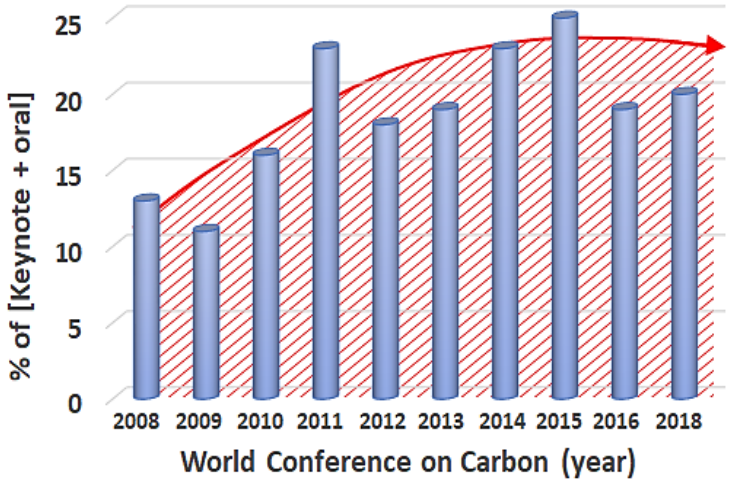


**Figure 1.** Evolution of the relative importance of the topic on "Electrochemical Applications*", expressed as the % of keynote+oral presentations on this topic, for the last 10 years of The World Conference on Carbon. *sometimes the Topic referred to as Energy storage and conversion, Energy, etc.; data of 2017 not available.

**Figura 1.** Evolución de la importancia relativa de la temática de "aplicaciones electroquímicas*", expresada como % de presentaciones tipo keynotes+orales sobre esta temática, durante los últimos 10 años en el congreso mundial de los materiales carbonosos. *adquiriendo en ocasiones otros nombres, como Almacenamiento y conversión de energía, Energía, etc.; datos del año 2017 no disponibles.

from the delocalized π electrons in condensed aromatic rings, as well as their dimensions, order and/or crystalline assembly. This and other characteristics, together with a variable electrochemical activity for different processes and reactions, make carbon materials exceptional candidates to be used as electrodes, electrocatalysts or electrocatalysts supports in multiple electrochemical applications.

The present and potential impact of electrochemical applications of carbon materials may be incalculable. From the scientific point of view, in the last 10 years the relative importance of the topic on "Electrochemical Applications" within The World Conference on Carbon has significantly grown and seems to stabilize (Figure 1). During this period (2008-2018), it has been considered the most, second most and third most relevant topic (in number or % of keynote + oral communications) in The World Conference on Carbon on 4, 4 and 1 occasions, respectively; thus, remarkably beating the other most important topics of this conference, such as nanocarbons, graphene or porous carbons. This work analyzes the contributions related to the Electrochemical Applications Topic presented in the last World Conference on Carbon 2018 in Madrid.

## 2. Electrochemical applications Topic in The World Conference on Carbon 2018

Last July 2018, the World Conference on Carbon was held in Madrid. As it can be observed in Figure 2A, the topic on "Electrochemical applications" was the major among the different types of communications, i.e. keynote, oral and poster communications. In fact, even two sessions of oral communications on this topic were simultaneously carried out in different rooms.

Among the different subjects on this topic, energy storage on supercapacitors (SCs) clearly prevailed, followed by energy storage in batteries (BATTs) and energy conversion in fuel cells (FCs) (Figure 2B). It is worthy to mention that one of the keynotes was dedicated to SCs and BATs, and another to electrocatalysis in FCs and $CO_2$ electroreduction, so they have been accounted as 0.5 in the figure. Details on the research of these 3 main applications are provided below (sections 3-5).

Other electrochemical applications of carbon materials arise also great interest (Figure 2B). The utilization of carbon materials in electrochemical (bio)sensors or as support of different electrocatalysts are among the most stablish ones. Particularly, the electro-reduction of $CO_2$ is currently on the rise, so part of the keynote lecture of Prof. Bandosz (see section 5) was related to the influence of nanopores to syngas and $CH_4$ formation. Other interesting topics deal with the use of electrochemical techniques to process carbon materials, like the electrochemical exfoliation of graphite or the electrochemical functionalization of carbon surfaces.

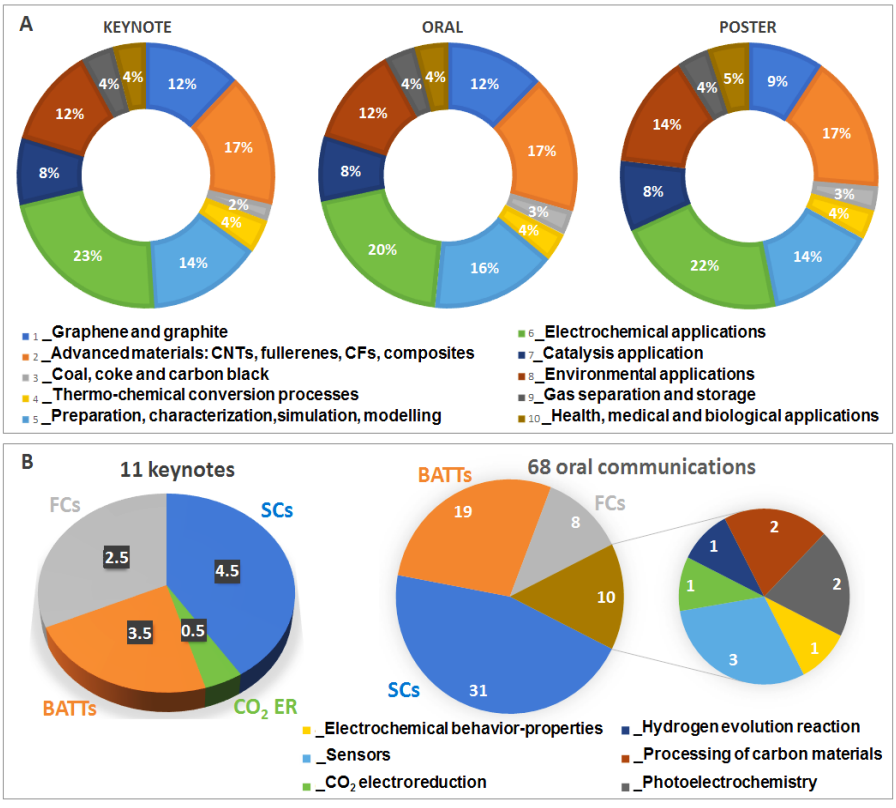


**Figure 2.** Distribution of (A) the different topics (%) and (B) the different electrochemical applications (number) within keynote-, oral- and poster-type communications in The World Conference on Carbon 2018.

**Figura 2.** Distribución de (A) las diferentes temáticas (%) y (B) las diferentes aplicaciones electroquímicas (número) en las comunicaciones tipo keynote, oral y póster en el congreso mundial de los materiales carbonosos 2018.

### 3. Research on Supercapacitors

The increase in energy density without compromising durability is one of the most challenging and hottest topics on SCs research. Significantly, the 4 keynote communications related to SCs in CARBON 2018 were devoted to this. Prof. Frackowiak (*Poznan University of Technology*) presented the latest results of her group on novel approaches for extending the capacitor voltage in aqueous electrolytes, including (i) the use of neutral electrolytes (sulfates, nitrates, iodides, etc.); (ii) selection of two different electrolytes (different pH) for positive and negative electrodes; and (iii) modifying the pH of positive and negative electrodes by ammonia treatment of carbon surfaces. Through these strategies, operating voltages of up to 1.8 V can be reached.

Major attention was paid into the study on ageing mechanisms of SC carbon electrodes, a topic that was the subject of two keynotes and part of the other two. Prof. Shiraishi (*Gunma University*) presented the last results on the durability and degradation mechanism of seamless AC electrodes in organic medium. Post mortem analysis of these electrodes indicated that the deposition of electrolyte decomposition products is the cause of the capacitance decline upon cycling at high voltage. On the other hand, the keynotes of Prof. Beguin (*Poznan University of Technology*) faced the study of this mechanism by electrochemical on-line (in-situ) mass spectroscopy, enabling to monitor the release of gases during operation. It was concluded that the ageing mechanism of electrodes strongly depends on the carbon material and the electrolyte type.

Nevertheless, the most represented subject on SCs (22 % of communications) tackled the preparation and study of nitrogen-doped carbon materials. N-functionalities have been proved to increase the pseudocapacitance, electrical conductivity or electrochemical stability of electrodes in these devices. In another keynote, Ms. M.J. Mostazo-López presented the collaborative research between the groups of Profs. Morallón and Cazorla-Amorós (both from *University of Alicante*) with Prof. Balducci (*CEEC, Jena*) that demonstrated the positive effect of these N-functionalities on the durability of high surface area (capacitance) AC in non-conventional electrolytes with large operation voltage, like Pyr14BF4/PC and Pyr14TFSI/PC.

On the other hand, other relevant research topics on SCs are the preparation and electrochemical characterization of novel electrode materials from biomass (21 % of communications) and composites (11 % of communications); or the study of ion adsorption on nanopores during charge/discharge (15 % of communications). Related to this last topic, it can be stressed the research on carbide-derived carbon materials, and the benefits of N-doping when used in ionic liquid (EMIM-$BF_4$), presented in a keynote by the group of Prof. Presser (*Saarland University*); and the new findings on the anomalous co-ion association of ionic liquids in carbon nanopores.

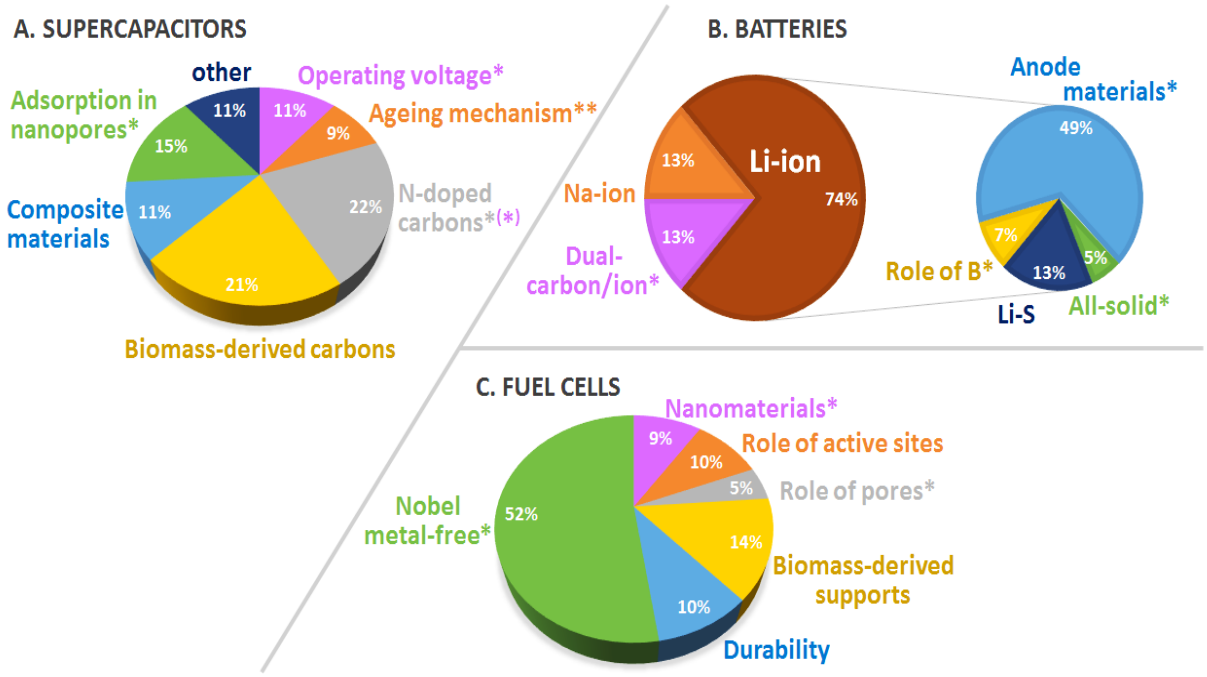


**Figure 3.** Distribution of different research subjects (%) among the keynote + oral communications on supercapacitors (A), batteries (B) and fuel cells (C) in The World Conference on Carbon 2018. Asterisks refer to keynote presentations, which may involve one or two different research subjects.

**Figura 3.** Distribución de diferentes temas de investigación (%) en las comunicaciones tipo keynote y orales sobre supercondensadores (A), baterías (B) y pilas de combustible (C) en el congreso mundial de los materiales carbonosos 2018. Los asteriscos hacen referencia a presentaciones tipo keynote, que pueden abarcar uno o dos temas de investigación distintos.

## 4. Research on Batteries

Regarding the application of carbon materials in batteries (Figure 3B), most research (ca. 75 %) is related to lithium-ion batteries (LIBs), which currently constitute the state-of-the-art technology for various small-scale and large-scale applications. Within this field, the design and study of new anode materials is the major focus of research (49 %). In their keynote presentation, the group of Prof. Presser showed the performance of silicon oxycarbides (SiOC) as anode material for LIBs, exhibiting high capacities (up to 922 mAh/g) and capacity retentions (83% after 100 cycles). In another keynote, Prof. Kawaguchi (Osaka Electro-Communication University) presented recent results on the electrochemical intercalation of Li into B-doped carbon materials. Different techniques reveal an interaction between intercalated Li ions and B atom, so these materials can show higher reversible capacity (up to 540 mAh/g) and the higher rate capability than commercially available graphite.

Moreover, advanced LIB technologies always receive great expectation. In a keynote communication, the group of Prof. Moriguchi (Nagasaki University) analyzed the charge/discharge properties of $SnO_2$-embedded nanoporous carbons in all-solid-state LIBs. Other works were dedicated to the lithium sulfur (Li-S) battery systems, using novel carbon-sulfur based cathode materials, which potentially offer significant advantages over metal oxides-based LIBs for high-energy density storage devices.

On the other hand, the conference witnessed the growing interest in alternative battery technologies with advantages in terms of cost and sustainability, such as Na-ion batteries and the so-called dual-ion or dual-carbon batteries (with 13 % of communications both). In the case of Na-ion batteries, most work is devoted to the study of anode materials, e.g. hard carbons. Respect to dual-ion or dual-carbon batteries, the group of Prof. Winter (University of Münster) presented an overview on the promises, challenges and limitations of this technology. Besides, in a keynote communication, they analyzed the effect of the graphitization degree of non-graphitic and graphitic carbons on their anion uptake capability as cathodes for dual-ion batteries. It has been found that the specific discharge (de-intercalation) capacity remarkably increases with the degree of graphitization.

## 5. Research on Fuel Cells

CARBON 2018 compiled an outstanding progress on fundamental-mechanistic aspects for the Oxygen Reduction Reaction (ORR) catalyzed by carbon materials. Thus, two keynotes and one oral communications were dedicated to study and discuss the role of pores, N-doping and active sites, respectively, on the ORR performance.

Prof. Bandosz (*The City College of New York*) emphasized the role of nanopores in the ORR for carbon free of heteroatoms and metals. The onset potential of the ORR was found to depend on the size of ultramicropores. An enhancement in the ORR performance owing to adsorption forces in small pores was concluded and the involved mechanisms were discussed.

Dr. D. Sebastián presented the advances of the group of Prof. Lázaro (*Instituto de Carboquímica*) on noble metal-free electrocatalysts based on N-doped carbon. They effect of N content on the ORR activity of metal-free or M (Co or Ti)-doped reduced graphene oxide (rGO) was analyzed. An optimum nitrogen doping of ca. 10 wt.% was found, and the presence of transition metals (Co and Ti) synergistically contributed to the positive shift of potential for ORR.

A systematic study on the influence of active sites on a wide range of different metal- and heteroatoms-free carbon materials was presented by Dr. A. Gabe from the groups of Profs. Morallón and Cazorla-Amorós (*University of Alicante*). A linear relationship between ORR activity and carbon-oxygen gasification reactivity was found, emphasizing the effect of the active surface area (ASA).

Apart from the significance of these fundamental works, most communications in the field of fuel cells were focused on the preparation and characterization of novel ORR electrocatalysts (Fig. 3C), highlighting metal noble-free and N-doped carbons (with 52 % of communications) and the development of simpler synthetic methods and/or by using more sustainable carbon precursors (14 % of communications). Moreover, a keynote by Prof. Mingbo Wu (*China University of Petroleum*) was related to the electrocatalytic performance of petroleum coke-based carbon nanomaterials.

## 6. Conclusions

The analysis of the contributions on *Electrochemical Applications Topic* presented in the last World Conference on Carbon 2018 indicates that: (i) the increase in energy density through different strategies, highlighting the use of N-doped carbons, the analysis of ageing mechanisms and the development of biomass-derived carbon electrodes prevail in SCs research; (ii) the design and study of new anode materials for LIBs dominates the research on batteries, while emerging Na-ion and dual-ion or dual-carbon technologies present promising perspectives to solve some of the problems associated to LIBs; (iii) related to FCs, the understanding of the role of pores, N-doping and active sites on the ORR performance of carbon materials has been greatly progressed.