

Review of Carbon Materials: Application in Alternative Energy Sources and Catalysis

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Abstract—The application of carbon materials in the branches of the electrochemical industry shows an increasing tendency each year due to the many interesting properties they possess. These are, among others, a well-developed specific surface, porosity, high sorption capacity, good adsorption properties, low bulk density, electrical conductivity and chemical resistance. All these properties allow for their effective use, among others in supercapacitors, which can store electric charges of the order of 100 F due to carbon electrodes constituting the capacitor plates. Coals (including expanded graphite, carbon black, graphite carbon fibers, activated carbon) are commonly used in electrochemical methods of removing oil derivatives from water after tanker disasters, e.g., phenols and their derivatives by their electrochemical anodic oxidation. Phenol can occupy practically the entire surface of carbon material and leave the water clean of hydrophobic impurities. Regeneration of such electrodes is also not complicated, it is carried out by electrochemical methods consisting in unblocking the pores and reducing resistances, and thus their reactivation for subsequent adsorption processes. Graphite is commonly used as an anode material in lithium-ion cells, while due to the limited capacity it offers (372 mAh g^{-1}), new solutions are sought that meet both capacitive, efficiency and economic criteria. Increasingly, biodegradable materials, green materials, biomass, waste (including agricultural waste) are used in order to reuse them and reduce greenhouse effects and, above all, to meet the biodegradability criterion necessary for the production of lithium-ion cells as chemical power sources. The most common of these materials are cellulose, starch, wheat, rice, and corn waste, e.g., from agricultural, paper and pharmaceutical production. Such products are subjected to appropriate treatments depending on the desired application (including chemical, thermal, electrochemical). Starch is a biodegradable polysaccharide that consists of polymeric units such as amylose and amylopectin that build an ordered (linear) and amorphous (branched) structure of the polymer. Carbon is also used as a catalyst. Elemental carbon has become available in many nano-structured forms representing the hybridization combinations found in the primary carbon allotropes, and the materials can be enriched with a large number of surface functional groups. There are many examples of catalytic applications of coal in the literature, but the development of this field has been hampered by the lack of a conceptual approach combining structure and function and a lack of understanding of material synthesis. In the context of catalytic applications, the integrity of carbon environmental management properties and parameters such as metal conductivity range and bond sequence management should be characterized. Such data, along with surface and textured information, can form the basis for the provision of network support services.

Keywords—Carbon materials, catalysis, BET, capacitors, lithium ion cell.

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I INTRODUCTION

THANKS to the widespread use of hard coal in Poland, many people deal with it on a daily basis. Many kilograms of fuel are bought before the heating season. The properties of hard coal make it possible to obtain (thanks to gasification, hydrogenation or smelting) coke, various types of engine fuels and fuel gas or benzene. The metallurgical industry cannot do without it, it is used in the production of cosmetics, medicines, and even in the jewelry industry.

Activated carbon is also an ingredient in whitening toothpastes. Due to the content of tannins, such a paste helps to remove discoloration resulting, for example, from frequent drinking of coffee or tea. In addition, activated charcoal in toothpaste helps to eliminate unpleasant smell from the mouth and soothes irritated gums. It is worth adding that the mentioned properties of activated carbon can also be used by crushing the tablet into a brush, but remember not to use it too often, as it may damage the enamel.



Fig. 1 Application of carbon materials

Carbon is also used in the production of protective mask inserts and in the production of water and air filters. It is also used for the clarification of protein hydrolysates, musts, wines and juices, for the production of spirit, pure sugar, for the separation of gas mixtures, for the purification of vapors and gases. On the other hand, very black varieties of activated carbon are used for coloring.

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II CARBON IN SUPERCAPACITORS: OVERVIEW

Recently, electrochemical capacitors have attracted increasing attention due to the rapidly growing need for clean energy sources, as it can provide high power density, fast charge/discharge rate and long cycle lifetime. Electrochemical double layer capacitors (EDLCs) using carbonaceous materials as electrodes are extensively developed due to their low cost and high operation stability. Among them, carbon with large specific surface area is widely employed. However, its poor conductivity arising from non-graphitized structure has limited its charge/discharge performance at high charge/discharge current densities.

The value of specific surface area of carbon materials is limited by the thickness and specific weight of each layer of carbon. The maximum specific surface area of carbon materials is about $2600 \text{ m}^2 \text{ g}^{-1}$ [1]. However, they are found in the literature reports of carbon materials having a specific surface area of the order of $2900 \text{ m}^2 \text{ g}^{-1}$ [2], of $3000 \text{ m}^2 \text{ g}^{-1}$ [3]-[5], and even in the range $3200\text{-}3487 \text{ m}^2 \text{ g}^{-1}$ [6]-[9], which is caused method of determining (BET adsorption isotherm N_2). There are many reports in the literature regarding EDLC capacitors which show the possibility to use for the construction of different carbonaceous materials such as activated carbons in powder form [10], [11], carbon materials obtained from carbides [12], [13], woven carbon fiber [14], [15], carbon nanofibers [16], [17], carbon onions [18], carbon nanotubes [18]-[20], the carbon nanospheres, etc. It should be noted that the capacity of the carbon/electrolyte is usually given terms of carbon, with the simultaneous assertion that the coals "have the capacity". This statement is wrong, the more that highly porous carbon electrodes have a lower mass than the electrolyte contained in them [1].

The popularity of carbon as an electrode material is due to its chemical and physical properties, namely:

- high temperature stability
- controlled pore structure
- processability and compatibility in composite materials
- relatively low cost
- good conductivity

Carbon materials are often used electrode materials in the construction of electrochemical capacitors. As is known, the ability to conduct electric current is due to the presence of graphene planes in which the carbon atoms C have sp^2 hybridization (as opposed to non-conductive carbon varieties sp^3). The graphite resistance is high and depends on the structure and porosity. Carbon electrodes are available with a surface area of up to $2500 \text{ m}^2/\text{g}$. Carbon material is used in the form of powder, fabrics, felt or fibers. Electricity storage on carbon electrodes is capacitive in an electrochemical double layer. These are the so-called electrochemical EDCL capacitors. Progress in the field of nanotechnology allows us to predict that in the coming years the use of carbon nanomaterials heads in the form of single and multi-wall nanotubes or nanoparticles will allow for better results in relation to the specific capacity of the electrode materials.

III GRAPHITE- IMPORTANT MATERIALS

The technological industry, especially the electrochemical industry, enables the use and dissemination of various allotropic types of carbon. Electrodes used in electrochemical energy sources require a large amount of conductive carbon - in order to maintain proper conductivity [21], [22].

Graphite ceases to fulfill its role as an active material in lithium-ion cells due to intensified intercalation and other solutions are sought [21], [22]. Graphite is often used to dope the dry mass during the formation of the electrode paste to increase the stability of the material. The greatest development of carbonaceous materials in lithium-ion cells concerns their use as an anode active material or as a cathode conducting solvent [23]. Carbon anode materials include: HOPG (highly oriented pyrolytic graphite), natural graphite, artificial (synthetic) graphite, hard and soft carbons, carbon nanotubes, materials with low mesophase temperature and MCMB (mesocarbon microspheres) [21], [23]. Hard carbons show the greatest possible capacity. Outstanding performance, flat discharge profile, high operating voltage, significant efficiency (also at low temperatures) and electrical conductivity are observed for synthetic graphite. It is also characterized by a low cost [23]. Mesophasic carbon fibers (MCFs), e.g., Melbon 3100, exhibit a radial crystal orientation. This allows for the trouble-free insertion of lithium ions on either side of the material surface. The sidewall is covered with a thin, porous, graphene layer. It protects the fibers from changing shape during swelling and volume reduction. Fibers reaching a thickness of $7 \mu\text{m}$ are used in anodic coating systems. Toshiba uses fibers from 1 mm to 7 mm thick and the batteries thus created show excellent low temperature performance compared to conventional lithium-ion cells. Acetylene or carbon black also finds applicability, while it is characterized by a lower but satisfactory effectiveness and an initial irreversible capacity [23]. Carbon mesophase microspheres (MCMB), manufactured by Osaka Gas Co., are highly effective and can be easily applied to copper anode collectors. The price and the production process still require optimization due to the huge volume of solvent needed to wash and recover the beads from the division matrix [23].

IV HARD CARBONS

Hard carbons are formed when thermosetting resins are heated from materials such as sugars, proteins, cellulose. The process takes place under vacuum or inert gas. As a result of thermal decomposition, water and gases are released (syneresis). Then, the appropriate structure of carbon is obtained, the particles of which aggregate, creating a complex structure unable to transform into the form of graphite. The product shows high hardness, graphite structure and voids. Their significant advantage is the inability of these forms to decompose PC (propylene carbonate) used as a solvent. Its disadvantage is decomposition with the release of a large amount of heat in the presence of lithium graphite. A favorable phenomenon is the slight change in volume during the loading and unloading processes. It should be noted that due to slow

diffusion during reversible intercalation, hard carbons show little efficiency. Sony uses hard carbons in the anodes due to the increased lifetime of the cells. Replacing metallic lithium with carbon in Li-ion is to significantly increase the safety of battery use. The main distinguishing feature of such a solution is the possibility to control the formation of the passive SEI layer on the anode (Solid Electrolyte Interphase) on carbon or graphite at a specified time. It is impossible with metallic lithium. The SEI coating is usually formed during the first charging cycle. The revision of its formation and destruction is crucial for best battery performance and safety [23].

In recent years, attempts have been made to dope carbon with boron. The unique properties of boron, such as the introduction of additional electronic acceptor levels by its atoms, increase the specific capacities [23]. CNTs carbon nanotubes are innovative. They are made of rolled graphene layers, significantly resembling building bricks. Configuratively, they create the form of a chair, rectal and chiral. The use of CNTs allows to increase the specific surface area of the adsorbent, co significantly improves electrochemical applicability. Depending on the degree of graphitization, the SWCNT variant (single-walled) and carbon nanotubes with higher capacity than MWCNT (multi-walled) graphite are used. SWCNTs have a lithium reversible capacity of 460 mAh g⁻¹, while MWCNTs have up to 980 mAh g⁻¹.

V ACTIVATED CARBONS

Due to high surface area activated carbons in electrochemical capacitors can be stored a large amount of cargo. Activated carbons are characterized by good electrical conductivity and electrochemical stability. Electrical double layer can be formed rapidly, hence the electric double layer capacitors, characterized by a rapid increase in power compared to conventional batteries, for which may be a limiting factor in the faraday reaction kinetics. Also, the chemical properties of the electrodes of the capacitor, such as the distribution of functional groups on the surface of carbon electrodes, affects the performance of the capacitors, which share a certain faraday reaction [24]-[27].

M. Nakamura et al. [27] have studied the effects of physical properties of activated carbon on the properties of the electrical double layer of capacitor. The authors showed that the rest potential of the activated carbon is proportional to the logarithm of the oxygen content or the concentration of the acid functional groups on the surface of activated carbon.

According to the IUPAC classification of porous structure of activated carbons, it can distinguish three types of pores: micropores (pore diameter 1 nm or 2 nm), mesopores (with a diameter of 2-50 nm) and macropores (diameter above 50 nm). For most activated carbons total macropore part of the surface is negligible and is less than 2 m² g⁻¹. A significant portion of the surface of activated carbons are micropores that due to the small diameter may not be available for the electrolyte ions.

Theoretically, the larger the surface area of the activated carbon, the greater the obtained specific capacitance of the capacitor.

VI CARBON NANOTUBES

Carbon nanotubes (CNTs) can be distinguished as: single-walled carbon nanotubes SWCNT [28]-[32], double-walled carbon nanotubes DWCNT [33], [34], multi-walled carbon nanotubes MWCNT [35]-[40], fluoridated FCNT carbon nanotubes [41], as well as activated carbon nanotubes ACNT [42], [43].

Carbon nanotubes have high mesoporous, easy accessibility for the electrolyte ions and excellent electrical conductivity.

Recently, the electric double layer capacitor (EDLC) has attracted extensive interest because of its advantages such as fast charge-discharge rate, high power-density in discharging and recharging, excellent cycle lives on the order of 10⁵ to 10⁶, many times those of batteries, and environmental friendliness [44]-[46]. Surface active carbon materials are recognized as an essential component for EDLC. EDLC properties have recognized to depend strongly upon physicochemical properties such as surface area and pore size of carbon materials [47], [48], precursor of carbon materials for carbon electrode [49], [50].

Various carbon materials could be used as supercapacitors electrodes, typical examples include carbon nanotubes (CNTs) [51], [52] and ordered mesoporous carbon (OMC) [53], [54]. CNTs are used as electrodes to increase the power density as a result of their unique tubular structures and superior electrical properties, which favor fast ions and electrons transportation. However, the high production cost and entanglement problem limit their wide spread applications [55], [56]. OMC possesses excellent electrochemical performance due to its high surface area, narrow pore size distribution and uniform pore connection. But the conventional hard-template nanocasting method to prepare OMC is obviously high-cost. Modifications of carbon materials are very important due to the use of a given material and due to its electrochemical performance. Hence the advantages and disadvantages very often.

VII CARBON AEROGELS, XEROGELS AND CROGELS

Organic aerogels CA (specific surface area > 400 m² g⁻¹), consisting of interconnected colloidal particles, plates or fibers, are obtained resin: resorcinol-formaldehyde, cresol-formaldehyde, phenol-resorcinol-formaldehyde, phenol-furfural, melamine-formaldehyde, polyurethanes and polyureas. The structure of the carbon airgel consists of a three-dimensional network of interconnected nano-particles having a diameter of 5-10 nm [57], [58].

Organic aerogels pyrolyzed under an inert atmosphere gives the carbon aerogels monolithic form, a powder, microspheres or in the form of composite thin films. The monolithic carbon airgel structure, relatively high specific surface area and electrical conductivity make carbon aerogels may be used in electrical double layer capacitors. The structure and properties of the carbon airgel depend on the synthesis conditions, the pyrolysis temperature, the presence of dopant activation.

Literature review of electrochemical capacitors in which the electrode material as aerogels have been used (CA), cryogels (CGC) and carbon xerogels (XGC) are summarized in Table I.

TABLE I
LITERATURE REVIEW OF THE ELECTRIC DOUBLE LAYER CAPACITOR AS AN
ELECTRODE MATERIAL CONTAINING AEROGELS, CRYOGELS AND XEROGELS
CARBON [59]-[68]

Electrolyte	Electrode	Counter-electrode
4M KOH	CA	CA
1M H ₂ SO ₄	CA+RuO ₂	G
5M KOH, 0,5M Et ₄ NBF ₄ in PC	CA	CA
30% H ₂ SO ₄	CA	CA
4M KOH	ACA	ACA
1M H ₂ SO ₄	CA	CA
1M H ₂ SO ₄	CA	Pt
1M H ₂ SO ₄	PAN-CA	Pt
1M H ₂ SO ₄	CA	Pt
aqueous solution NaF	CA	CA2
6M H ₂ SO ₄	CA	CA
0,8M Et ₄ NBF ₄ in PC	AC or CA	AC or CA
0,8M Et ₄ NBF ₄ in PC	CA	CA
30 wt.-% KOH	CA	CA
1,5M Et ₃ MeNBF ₄ in PC	CA (surfactant)	CA (surfactant)
6M KOH, 1M Na ₂ SO ₄ , 2M (NH ₄) ₂ SO ₄	CA	CA
PVA-KOH lub 6M KOH	CA	CA
1M Et ₄ NBF ₄ in PC	ACA (surfactant) or CA	ACA (surfactant) or CA
30% KOH	CA	CA
0,8M Et ₄ NBF ₄ in PC	AC (surfactant) CA (surfactant)	AC (surfactant) CA (surfactant)
BMPyrNTf ₂ , EMImNTf ₂	XGC, CGC	pMeT
BMPyrNTf ₂ , EMImNTf ₂	XGC, CGC	Ag
1M H ₂ SO ₄	CA/SnO ₂	CA/SnO ₂
1M Et ₄ NBF ₄ w PC	CA/AC	CA/AC
1,5M Et ₃ MeNBF ₄ in PC	CA	CA
1,5M Et ₃ MeNBF ₄ in PC	CA	CA
30% KOH	CA	CA
1M H ₂ SO ₄	NCA	Pt
EMImNTf ₂ , BMPyrNTf ₂	XGC	XGC
4M KOH	CA	G
30% KOH	ACA	ACA

CA - carbon aerogel, G - graphite, PC - propylene carbonate, PAS - poly (acrylonitrile), AC - activated carbon, ACA - activated carbon airgel, pMet - poly (3-methylthiophene), XGC - carbon xerogel, CGC - carbon cryogel NCA - carbon airgel enriched with nitrogen

VIII CATALYSIS

The rapid development of modern society is based on massive energy consumption. However, the over-extraction and use of conventional fossil fuels leads to increasing environmental problems and problems related to the energy crisis. It is essential to search for sustainable and environmentally-friendly sources of energy. Due to its high heat of combustion and clean combustion product, hydrogen is considered a very promising energy carrier. As a clean and carbon neutral strategy, the Electrocatalytic Hydrogen Release (HER) reaction plays an important role in generating high purity hydrogen energy and potential in combination with renewable resources such as solar, wind and hydro power. The production of renewable energy, the extraction of chemical raw materials and the production of functional material from biomass in bulk are a promising direction of research. It is one of the important industrial methods of converting plant biomass

to produce commercial activated carbon with adsorptive properties and supports for heterogeneous active ingredients of the catalyst. It is worth noting that catalytically active material derived from biomass will be beneficial in creating a perfect, consistent cycle system. Plant biomass components, especially structural uniqueness, provide rich development space for the design of efficient active catalysts for the conversion and storage of renewable energy. Nanocarbon catalysts with structures regulated at the atomic-molecular level, excellent electronic conductivity, customizable physicochemical properties and solid mechanical-chemical stability show a promising potential for building an efficient catalytic system.

To achieve high efficiency of HER catalysts, three key factors must be taken into account: the number of active sites, the intrinsic activity of each active site, and electrical conductivity. Due to the abundance of earth and excellent electrical conductivity, carbon materials have attracted a lot of attention, especially the emergence of novel advanced carbon materials such as graphene, carbon nanotubes, etc. These properties, developed surface, electrochemical stability and nanostructures are features that contribute to their use as electrocatalysts [69]-[72].

IX CONCLUSION

One of the greatest achievements of modern nanotechnology is invention materials that were used to build supercapacitors, also called ultracapacitors or double layer capacitors. The prefix "super" was used in the name of these capacitors due to their large capacity. It decides about the effective surface of the electrodes and a very small distance between them.

The electrodes are made of electrically conductive activated carbon, the structure of which resembles a sponge. Such large surfaces with little material are obtained thanks to the use of carbon nanotubes, which are the main compound building electrodes in a supercapacitor.

Carbon nanotubes are cylindrical forms in the hollow tubes of nanometer size made of coiled carbon graphene (monatomic graphite layer). They are placed on one plane supermolecular structures. Nanotubes have a large surface area and high electrical conductivity, so they can be used in construction nanoelectrodes in a supercapacitor. They are excellent heat conductors. Bindings the bonds that make up the diamond, which is why they show enormous tear resistance.

Electrochemical capacitors using the so-called pseudocapacity redox is the second type of condensation electrochemical tracks widely used in practice. These are the so-called redox electrochemical capacitors or redox supercapacitors. These devices, apart from using the electric charge of the double layer, are a source of current from charge transfer reaction, concerning substances adsorbed on the surface and undergoing transformation in its Faradayan nature. The difference between the usual redox reaction and the discussed phenomenon is the availability of the substrate. In capacitors, the charge transfer is strictly limited to the electrode surface. The process takes place in many electrons and in a wide range of potentials. In this type of devices, it uses there are

materials capable of undergoing redox surface reactions (e.g., ruthenium oxides, electroactive polymers).

Graphite and its derivatives are characterized by good biocompatibility. Therefore, much attention is paid to research aimed at the use of nanotubes and graphene in sensors for determining the concentration of active substances in drugs, e.g., paracetamol, and biomarkers in biological matrices. As shown, the detection of compounds of physiological importance, e.g., dopamine, ascorbic acid and uric acid, can take place without the participation of enzymes. Parallel to this research, prototypes of enzymatic biomarker sensors are being constructed, in which the proteins responsible for catalyzing the redox reactions of analytes (oxidase and dehydrogenase) are deposited on nanotubes or graphene. Carbon nanotubes and graphene provide a good platform to directly study the mechanisms of redox reactions involving proteins such as myoglobin, hemoglobin and glucose oxidase. It has been observed that in the case of a graphene electrode or a carbon nanotube, it is possible to transfer an electron between the electrode and the protein without intermediating substances. It is very important from the point of view of research on the kinetics of reactions responsible for the occurrence of life processes.

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REFERENCES

- [1] A. Lewandowski, M. Galinski, *J. Power Sources* 173 (2007) 822.
- [2] G. Chun-yu, W. Cheng-yang, *Compos. Sci. Technol.* 67 (2007) 1747.
- [3] L. Wang, M. Fujita, M. Inagaki, *Electrochim. Acta* 51 (2006) 4096.
- [4] D.-W. Kim, J. M. Ko, W. J. Kim, J. H. Kim, *J. Power Sources* 163 (2006) 300.
- [5] W.-J. Kim, D.-W. Kim, *Electrochim. Acta* 53 (2008) 4331.
- [6] H. Zhang, W. Zhang, J. Cheng, G. Cao, Y. Yang, *Solid State Ionics* 179 (2008) 1946.
- [7] M. S. Balathanigaimani, W.-G. Shim, M.-J. Lee, Ch. Kim, J.-W. Lee, H. Moon, *Electrochem. Commun.* 10 (2008) 868.
- [8] B. Xu, F. Wu, R. Chen, G. Cao, S. Chen, Z. Zhou, Y. Yang, *Electrochem. Commun.* 10 (2008) 795.
- [9] V. Khomenko, E. Raymundo-Piñero, F. Béguin, *J. Power Sources* 177 (2008) 643.
- [10] W. Quiao, S.-H. Yoon, I. Mochida, *Energ. Fuels* 20 (2006) 1680.
- [11] K. Yuyama, G. Masuda, H. Yoshida, T. Sato, *J. Power Sources* 162 (2006) 1401.
- [12] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P.L. Taberna, *Science* 313 (2006) 1760.
- [13] J. A. Fernández, M. Arulepp, J. Leis, F. Stoeckli, T. A. Centeno, *Electrochim. Acta* 53 (2008) 7111.
- [14] A. Lewandowski, A. Olejniczak, *J. Power Sources* 172 (2007) 487.
- [15] I. V. Sheveleva, L. A. Zemskova, S. V. Zhelezov, A. Voit, N. N. Barinov, S. V. Sukhoverstov, V. I. Sergienko, *Russ. J. Appl. Chem.* 80 (2007) 924.
- [16] C. Merino, P. Soto, E. Vilaplana-Ortego, J. M. Gomez de Salazar, F. Pico, J. M. Rojo, *Carbon* 43 (2005) 551.
- [17] S.-H. Yoon, S. Lim, Y. Song, Y. Ota, W. Qiao, A. Tanaka, I. Mochida, *Carbon* 42 (2004) 1723.
- [18] C. Portet, G. Yushin, Y. Gogotsi, *Carbon* 45 (2007) 2511;
- [19] B.-J. Yoon, S.-H. Jeong, K.-H. Lee, H.S. Kim, Ch. G. Park, J. H. Han, *Chem. Phys. Lett.*, 388 (2004) 170.
- [20] C. Du, J. Yeh, N. Pan, *Nanotechnology* 16 (2005) 350.
- [21] L. S. Roselin, R. Shin Juang, C.-T. Hsieh, S. Sagadevan, A. Umar, R. Selvin, H. Hegazy, *Materials* 12 (2019) 1229
- [22] M. Salamia, H. Louis, S. Zafar, O. O. Amusan, *Asian Journal of Nanoscience and Materials* 2(1) (2018) 1-26
- [23] H. J. Santner, K. C. Möller, W. Kohs, C. Veit *Springer* (2006) 161-167, 157
- [24] M. Ishikawa, A. Sakamoto, M. Morita, Y. Matsuda, K. Ishida, *J. Power Sources* 60 (1996) 233.
- [25] A. Yoshida, S. Nonaka, I. Aoki, A. Nishino, *J. Power Sources* 60 (1996) 213.
- [26] H. Shi, *Electrochim. Acta* 41 (1996) 1633.
- [27] M. Nakamura, M. Nakanishi, K. Yamamoto, *J. Power Sources* 60 (1996) 225.
- [28] T. Liu, T.V. Sreekumar, S. Kumar, R.H. Hauge, R.E. Smalley, *Carbon* 41 (2003) 2427.
- [29] C. Zhou, S. Kumar, C.D. Doyle, J.M. Tour, *Chem. Mater.* 17 (2005) 1997.
- [30] C. Zhou, T. Liu, T. Wang, S. Kumar, *Polymer* 47 (2006) 5831.
- [31] J. Oh, M. E. Kozlov, B. G. Kim, H.-K. Kim, R. H. Baughman, Y.H. Hwang, *Synthetic Met.* 158 (2008) 638.
- [32] P. W. Ruch, R. Kötz, A. Wokaun, *Electrochim. Acta* 54 (2009) 4451.
- [33] C. Portet, P. L. Taberna, P. Simon, E. Flahaut, *J. Power Sources* 139 (2005) 371.
- [34] Y. Honda, M. Takeshige, H. Shiozaki, T. Kitamura, K. Yoshikawa, S. Chakrabarti, O. Suekane, L. Pan, Y. Nakayama, M. Yamagata, M. Ishikawa, *J. Power Sources* 183 (2008) 1580.
- [35] T. Bordjiba, M. Mohamedi, L.H. Dao, *J. Power Sources* 172 (2007) 991.
- [36] Ch.-Ch. Hu, J.-H. Su, T.-Ch. Wen, *J. Phys. Chem. Solids* 68 (2007) 2353.
- [37] Ch.-W. Huang, Y.-T. Wu, Ch.-Ch. Hu, Y.-Y. Li, *J. Power Sources* 172 (2007) 460.
- [38] Ch.-T. Hsieh, Y.-W. Chou, W.-Y. Chen, *J. Solid State Electrochem.* 12 (2008) 663.
- [39] W. Xing, S. Zhuo, H. Cui, W. Si, X. Gao, Z. Yan, *J. Porous Mat.* 15 (2008) 647.
- [40] J. P. Zheng, C. M. Pettit, P. C. Goonetilleke, G. M. Zenger, D. Roy, *Talanta* 78 (2009) 1056.
- [41] J. Y. Lee, K. H. An, J. K. Heo, Y. H. Lee, *J. Phys. Chem. B* 107 (2003) 8812.
- [42] Ch. Li, D. Wang, T. Liang, X. Wang, L. Ji, *Mater. Lett.* 59 (2004) 3774.
- [43] Q. Jiang, Q. Zhang, B. Du, R. L. Zou, Y. H. Liu, Y. Zhao, *J. Mater. Sci.: Mater. Electron* 19 (2008) 241.
- [44] H. Jiang, P. S. Lee, C. Z. Li, *Energy Environ. Sci.* 6 (2013) 41.
- [45] J. K. Miller, P. Simon, *Science* 321 (2008) 651.
- [46] G. P. Wang, L. Zhang, J. J. Zhang, *Chem. Soc. Rev.* 41 (2011) 797.
- [47] C. C. Hu, K. H. Chang, M. C. Lin, Y. T. Wu, *Nano Lett.* 6 (2006) 2690.
- [48] H. Jiang, T. Zhao, C. Z. Li, J. Ma, *J. Mater. Chem.* 21 (2011) 3818.
- [49] R. K. Paul, M. Ghazinejad, M. Penchev, J. Lin, M. Ozkan, S. Ozkan, *Small* 6 (2010) 2309.
- [50] Y. F. Yan, Q. L. Cheng, G. C. Wang, C. Z. Li, *J. Power Sources* 196 (2011) 7835.
- [51] J. P. Randin, E. Yeager, *J. Electroanal. Chem.*, 36,257 (1972).
- [52] J. P. Randin, E. Yeager, *Electroanalytical Chemistry and Interfacial Electrochemistry*, 58,313(1975).
- [53] S. Iijima, *Nature*, 354,56 (1991).
- [54] N. M. Rodriquez, *Mater. Res.*, 8, 3233 (1993).
- [55] B. E. Conway (Edior), *Electrochemical Suoercapacitors "Scientific fundamental and technological applications"*, p.12, Kluwer Acedamic/Plenum Publishers (1999).
- [56] C. Dekker, *Phys. Today*, 5, 22 (1999).
- [57] S-H. Yoon, A. Tanaka, S. Lim, Y. Korai, I. Mochida, B. Ahn, K. Yokogawa, C-W.Park, In *Processing of Carbon 2003. International Conference on Carbon, Oviedo, Spain, p76 (2003).*
- [58] S.-W. Hwang, S.-H. Hyun, *J. Non-Cryst. Solids* 347 (2004) 238.
- [59] L. Zhang, H. Liu, M. Wang, W. Liu, *Rare Metals* 25 (2006) 51.
- [60] H. Pröbstle, C. Schmitt, J. Fricke, *J. Power Sources* 105 (2002) 189.
- [61] B. Fang, Y.-Z. Wei, K. Suzuki, M. Kumagai, *Electrochim. Acta* 50 (2005) 3616.
- [62] B. Fang, Y.-Z. Wei, K. Maruyama, M. Kumagi, *J. Appl. Electrochem.* 35 (2005) 229.
- [63] J. M. Miller, B. Dunn, T. D. Tran, R. W. Pekala, *J. Electrochem. Soc.* 144 (1997) L309.
- [64] C. Schmitt, H. Pröbstle, J. Fricke, *J. Non-Cryst. Solids* 285 (2001) 277.
- [65] N. Yoshizawa, H. Hatori, Y. Soneda, Y. Hanzawa, K. Kaneko, M.S. Dresselhaus, *J. Non-Cryst. Solids* 330 (2003) 99.
- [66] H. Talbi, P.-E. Just, L. H. Dao, *J. Appl. Electrochem.* 33 (2003) 465.
- [67] H. Pröbstle, M. Wiener, J. Fricke, *J. Porous Mat.* 10 (2003) 213.

- [68] D. Kalpana, N. G. Renganathan, S. Pitchumani, *J. Power Sources* 157 (2006) 621.
- [69] C. Arbizzani, S. Beninati, M. Lazzari, F. Soavi, M. Mastragostino, *J. Power Sources* 174 (2007) 648.
- [70] H. Ren, Z.-H. Huang, Z. Yang, S. Tang, F. Kang, R. Lv, *J. Energy Chem.* 2017, 26, 1217– 1222
- [71] X. Wang, X. Gan, T. Hu, K. Fujisawa, Y. Lei, Z. Lin, B. Xu, Z. H. Huang, F. Kang, M. Terrones, R. Lv, *Adv. Mater.* 2017, 29, 1603617
- [72] Y. Lei, S. Pakhira, K. Fujisawa, X. Wang, O. O. Iyiola, N. Perea Lopez, A. Laura Elias, L. P. Rajukumar, C. Zhou, B. Kabius, N. Alem, M. Endo, R. Lv, J. L. Mendoza-Cortes, M. Terrones, *ACS Nano* 2017, 11, 5103–5112