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Lithium-Catalyzed Carbon Aerogel and Its Possible Application in Energy Storage Materials

MATEUSZ CISZEWSKI,[1,4] ELŻBIETA SZATKOWSKA,[2]
and ANDRZEJ KOSZOREK[3]

1.—Department of Hydrometallurgy, Institute of Non-Ferrous Metals, Sowińskiego 5, 44-100 Gliwice, Poland. 2.—Department of Production Engineering, University of Bielsko-Biala, Willowa 2, 43-309 Bielsko-Biała, Poland. 3.—Department of Inorganic, Analytical Chemistry and Electrochemistry, Silesian University of Technology, Krzywoustego 6, 44-100 Gliwice, Poland. 4.—e-mail: mateusz.ciszewski@imn.gliwice.pl

A lithium-based catalyst for carbon aerogel compounds and carbon nanotubes synthesis was used. Lithium hydroxide-catalyzed and CNT-modified carbon aerogel was compared to traditionally synthesized sodium carbonate-catalyzed carbon aerogel, as well as to the same material modified with CNT to evaluate the real effect of lithium hydroxide addition. Enhancement in the specific surface area from 498 m^2/g to 786 m^2/g and significant change in pore size distribution were observed. Low temperature, supercritical drying in carbon dioxide was used to prepare an organic aerogel with subsequent pyrolysis in an inert gas flow to convert it into carbon aerogel. The as-obtained material was examined with respect to energy storage applications, i.e. symmetric hybrid supercapacitors. It was shown that lithium hydroxide was responsible for shorter gelation time, increased specific surface area, and a greater number of micropores within the structure. For both reference materials prepared using sodium carbonate, quite different data were recorded. It was presented that the proper choice of carbon matrix should combine both high specific surface area and appropriate pore size distribution. High surface area and a relatively large number of micropores were responsible for specific capacity loss.

Key words: Carbon aerogels, supercritical drying, supercapacitors, lithium catalyst, CNT

INTRODUCTION

Carbon aerogels are a new class of compounds that can be considered for energy storage applications. This is because of their high surface area, low weight, tunable properties, and easy synthesis. The history of aerogels dates back to 1931 when Steven Kistler from the College of the Pacific in Stockton, California invented the first aerogel based on silica.[1] The first organic aerogel synthesis is attributed to Richard Pekala from the Lawrence Livermore National Laboratory in Berkeley, who obtained clusters of functionalized polymers by polycondensation of resorcinol with formaldehyde with subsequent supercritical drying.[2,3] The process is composed of several stages: gelation, aging, solvent exchange, drying, and pyrolysis. During gelation, resorcinol at first reacts with formaldehyde under alkaline or acid pH through CH_2 bridges; these resorcinol derivatives condense into clusters, and finally, they crosslink through CH_2OH groups into a gel.[4] Cluster formation is strongly dependent on pH, temperature, and concentration of reagents. The base catalyst is responsible for deprotonation of hydroxymethylated resorcinol, leading to a very reactive o-quinone methide intermediate formation. Gels can be divided into three main groups, namely, aerogels, cryogels, and xerogels based on drying method used, supercritical drying, freeze-drying and ambient pressure drying, respectively.

Even a very small difference in process conditions during gelation may significantly change the structure of product. Therefore, it is quite difficult to estimate the influence of the specific drying method on pore structure. The three main factors influencing texture and pore structure are resorcinol to formaldehyde ratio (R/F), dilution, i.e. the amount of water with respect to resorcinol + formaldehyde + catalyst, and catalyst amount that can be designated as R/C ratio.[5] Catalysts used in synthesis of carbon aerogels can be divided into either acidic or basic groups. The role of the catalyst is to keep an appropriate initial pH value that is the rate determining step and create an intermediate chelated form.[6] Metal salts are the most commonly used carbon aerogel catalysts, and sodium carbonate is the top rated. Using sodium carbonate, the carbon aerogel is able to have the specific surface area close to 620 m^2/g.[7] Metal hydroxides, namely, NaOH, KOH, LiOH, $Ca(OH)_2$, $Ba(OH)_2$, and $MgOH_2$ were also examined as possible catalysts in carbon aerogels synthesis.[8] It was found that cation radius and metal valence are key factors in catalyst choice. Divalent cations were responsible for faster formaldehyde consumption than monovalent; however, the most intriguing kinetics was observed for lithium, which is a monovalent atom, but behaves more like a divalent atom. The influence of chromium, molybdenum, and tungsten catalysts (in the form of chromium nitrate, ammonium heptamolybdate, and ammonium tungstate) was also examined in carbon aerogels.[9] The best results were obtained for tungsten. When ammonium tungstate was used as a catalyst the needle-like WO_3 homogenously distributed in carbon aerogels was produced.[10] Many others transition-metal catalysts such as Pt, Pd, Ag, Fe, Co, Cu have been studied in order to control and to improve the porous structure of the resultant carbon aerogels.[6] Magnesium acetate was also examined to produce robust frameworks and improved pore interconnectivity.[6] This catalyst resulted in an increased specific surface area and significantly bigger micropores volume of carbon aerogel in comparison to Na_2CO_3-catalyzed aerogel. Examples of other non-metal catalysts are acetic acid, hydrochloric acid, nitric acid, and hexamethylenetetramine.[11–13]

The quality determining factor of carbon aerogels is also pyrolysis, which converts organic aerogels into carbon aerogels. Generally pyrolysis is responsible for changing the specific surface area and conductivity of aerogels. Increase in pyrolysis temperature tends to reduce surface area; however, this effect can be observed at temperatures above 600°C. On the other hand, above 750°C electrically conductive materials can be obtained. This simply shows how hard it is to enhance both of these parameters. When pyrolysis temperature is above 1000°C graphite domains start to form.[4] In this paper an intriguing, and until now scarcely described in literature, lithium catalyzed carbon aerogel was prepared and then examined as potential material for energy storage demand.

EXPERIMENTAL DETAILS

CNT Preparation

Vertically aligned carbon nanotubes were obtained in a chemical vapor deposition process from toluene (HPLC grade, Fisher Scientific) as a carbon precursor and ferrocene (99.5%, Alfa Aesar) as a catalyst.[14] The specified amount of toluene was ultrasonicated with 3 wt.% ferrocene just before the process. The reaction was carried out in a horizontal furnace with three heating sections under argon atmosphere. CNTs were synthesized in Department of Materials Science and Metallurgy, Cambridge University.[3]

Carbon Aerogel Preparation

Carbon aerogels were synthesized using resorcinol (R), formaldehyde (F), water (W), and catalyst (C) in the following molar ratios: $R/F = 0.64$, $R/W = 0.056$, $R/C = 100$.[3] Additionally, 1 g (0.46 wt.%) of CNT was added to carbon aerogel–CNT samples. As a catalyst, lithium hydroxide, and comparatively sodium carbonate as a reference catalyst, were used. All components were magnetically mixed with 190 mL demineralized water at 500 rpm for 48 h and 72 h, in the cases of lithium hydroxide-catalyzed and sodium carbonate-catalyzed materials, respectively. Such a difference was caused by much faster gelation of lithium-based material. Then samples were poured into vials, sonicated for 15 min, closed, and kept at 80–85°C for 7 days. Next, the samples were cooled to room temperature and immersed in acetone for solvent exchange. Solvent was exchanged several times. During the first solvent exchange, 5% acetic acid was added to acetone to enhance crosslinking. As obtained gel was then put to autoclave (Lampart, 0.75 L, max. pressure: 450 atm., max. temperature 350°C) for CO_2 low temperature supercritical drying (LTSCD). Gel was dried with carbon dioxide for three days, gas was exchanged two times per day. During the last drying step, the temperature of the reactor was increased up to 70°C (the pressure inside reactor was 15 MPa), and maintained for 30 min. An exhaust valve was used to keep the pressure constant. Mass loss after drying was 76.82%, 84.77%, and 81.62% for CA, CA^{CNT}, and $CA^{CNT,Li}$, respectively.

Finally, carbon aerogels were carbonized in a tubular electric furnace at 900°C for 0.5 h under inert gas flow. Second mass loss was observed 40.96%, 52.71%, and 45.15%, respectively. Materials preparation was schematically presented in a Fig. 1.

Characterization

Brunauer Emmet Teller (BET) surface area and pore size distribution were analyzed using pore structure analyzer (3Flex^{tm}, Micromeritics) by means of Barrett-Joyner-Halenda method and t-plot. X-ray diffraction (XRD) analysis was
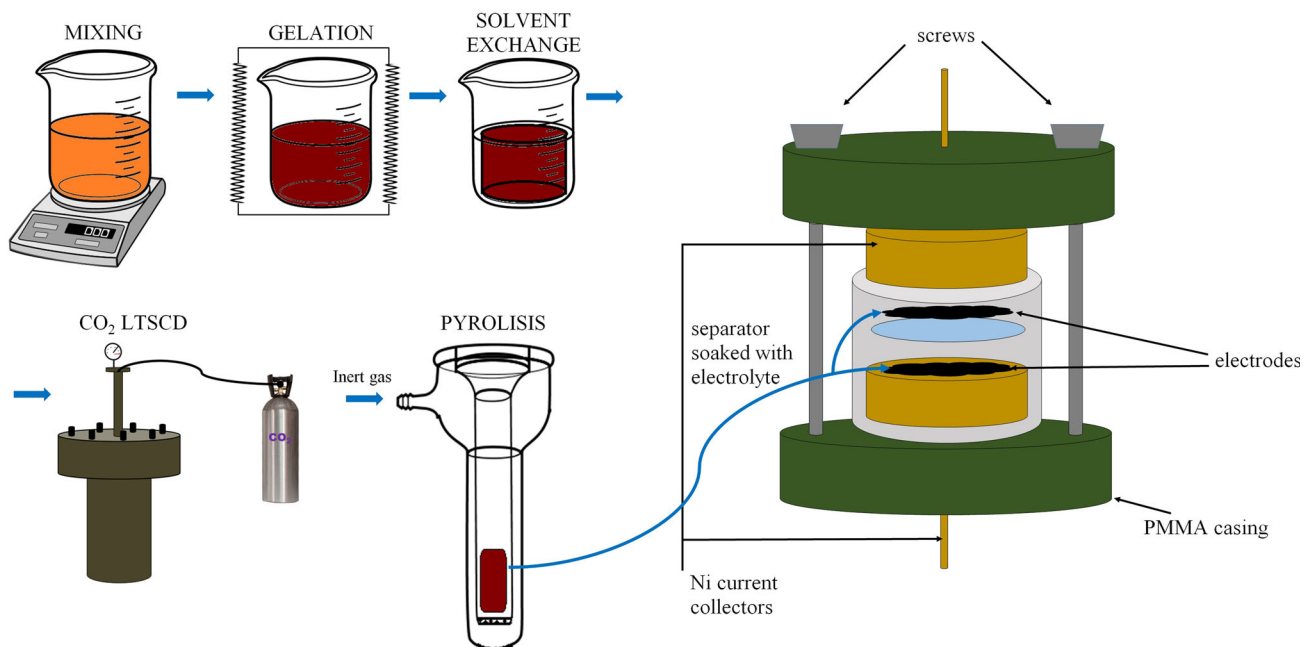
Fig. 1. Scheme of carbon aerogels synthesis and electrochemical tests assembly.

performed using Co Kα lamp in 2θ range from 10° to 100° (Seifert FPM). Electrochemical experiments were carried out using a two-electrode system. The working electrode materials were pasted on electrochemical nickel current collectors to form films and separated with membrane (Whatman) soaked with 6 M KOH. The accurate weight of the electrodes was read by a high-precision balance (Mettler Toledo AB 204S). Electrodes, current collectors, and separator were pressed by four screws in a poly(methyl methacrylate) casing. Cyclic voltammetry (CV) and galvanostatic charge/discharge (GC) characteristics were performed with Autolab PGSTAT 302N workstation.[3]

RESULTS

Anomalous behavior of the lithium catalysis of organic aerogel synthesis, which was mentioned in Introduction, required verification. This monovalent metal belongs to the same group of catalysts as potassium and sodium; however, the kinetics of catalysis more resembles divalent atoms. In this paper organic aerogel was synthesized using lithium hydroxide with a tiny amount of CNT to improve electric conductivity of the product. To observe a real effect of lithium catalyst, a similar material containing CNT was sythesized using typical aerogel catalyst–sodium carbonate. Comparatively bare aerogel was prepared without CNT

addition using only resorcinol, formaldehyde, water, and sodium carbonate.

All organic aerogels obtained were pyrolised and converted into carbon aerogels. It was noted that during homogenization (mixing of reactants) lithium hydroxide-catalyzed gel was very dense after about 48 h, while in the case of sodium carbonate it was 72 h for both bared gel and the CNT-modified one. The gelation time was 7 days in each case; however, the solution with lithium hydroxide gelled entirely after 5 days. Nevertheless, it was kept at elevated temperature for a longer time. This probably caused significant shrinkage of the material. This preliminary observation allowed us to determine that the lithium hydroxide-catalyzed carbon aerogel is much different than sodium carbonate aerogel.

One of the key factors in proper matrix material selection for supercapacitors is the specific surface area; therefore, this type of analysis was done first. It was noted that in the case of lithium hydroxide-catalyzed carbon aerogel the biggest specific surface area was obtained—ca. 786 m^2/g (Table I). Although both CNT-containing carbon aerogels had significantly increased BET surface area the calculated median pore width was in the same range for sodium carbonate-catalyzed aerogels regardless of whether these were modified by CNT or not. Median pore width defines the diameter for which one half of the pore volume is found to be in

Table I. Specific surface area and pore width for analyzed materials

	CA	CA^{CNT}	CA^{CNT,Li}
BET (m^2/g)	498.00	659.00	786.00
Median pore width (nm)	3.863	3.868	0.596

larger pores and one half to be in smaller pores. It was used to present better pore size variation in both materials. Carbon aerogel catalyzed with lithium hydroxide had much different and relatively small median pore width—close to 0.6 nm.

Unmodified, as well as CNT-modified carbon aerogels had a similar number of mesopores with some discrepancies in the number of micro- and macropores (Fig. 2). As is known, macropores are responsible for initial wetting of the electrode material and are said to be gates for molecules, while mesopores roles are both transportation canals and electrolyte containers within material. Therefore, it is required to have pores composed of some macro-gates and mesoporous channels. Micropores are very often too small for electrolytes and do not always participate in charge/discharge cycles in total. A quite different situation was observed for CNT–carbon aerogel prepared using lithium hydroxide. Much more micropores were created that probably resulted from fast gelation.

X-ray diffraction patterns recorded for CA, CA^{CNT}, and CA^{CNT,Li} were presented in a Fig. 3. It was found that all materials were strongly amorphous with two low intensity and broad signals emerged at 22°–30° and 48°–54°. As a Co Kα lamp was used in these analyses instead of the commonly applied Cu Kα lamp, peak shifts were observed of about 4°–5°. Both signals indicated a low degree of graphitization of examined carbon aerogels; however, in CA^{CNT} a small signal attributed to ordered graphitic domains was detected. Its localization was around 30° that corresponded to 26° graphitic domain signal in the case of the traditional Cu Kα lamp. It is suggested that an increase in pH caused by lithium hydroxide might influence structure disorder in comparison to the sodium catalyst, i.e. it was less probable to build up small graphitic-prone domains in more microporous material (CA^{CNT,Li}) than it was in mesoporous CA^{CNT}. After pyrolysis these bigger domains in CA^{CNT} resulted in more ordered structures with a signal ca. 30°.

Cyclic voltammetry curves (Fig. 4) obtained for all three materials at a scan rate 500 mV/s in a potential window 0–1 V showed really good charge–discharge characteristics with symmetric box-like shape. The most desired characteristics were obtained for lithium hydroxide-catalyzed carbon aerogels, i.e. there were not any peaks during cycling, and the current intensity during charging and discharging was slightly bigger. The loss in specific capacity for CA, CA^{CNT}, and CA^{CNT,Li} after
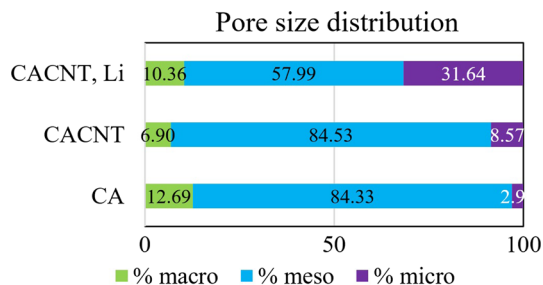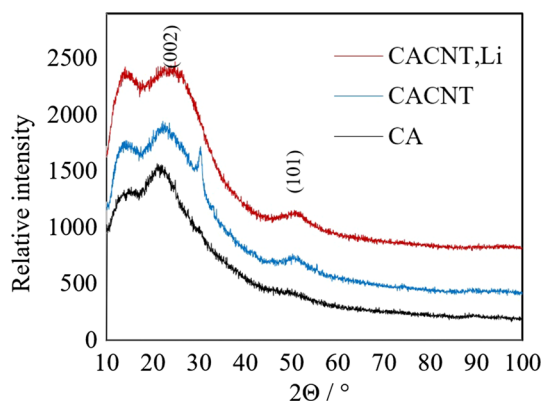

Fig. 2. Pore size distribution for all three carbon aerogels.

Fig. 3. XRD patterns obtained for CA, CA^{CNT}, and CA^{CNT,Li}.

1000 cycles was as high as 14.9%, 4.1%, and 11.0%, respectively.

The real value of specific capacity was calculated from galvanostatic charge discharge curves. Surprisingly, a common feature of incomplete discharge was observed for CA and CA^{CNT,Li}, while for CNT-modified carbon aerogel prepared using sodium carbonate, a symmetric characteristic was observed with complete and fast discharge. The calculated specific capacity for CA, CA^{CNT}, and CA^{CNT,Li} was 370 F/g, 226 F/g, and 194 F/g, respectively. It was obtained at current density 0.24 A/g for CA, 12 A/g for CA^{CNT}, and 0.6 A/g for CA^{CNT,Li}. The main reason for different current density applied was to use a fully accessible potential window for aqueous electrolyte. It should be noted that the specific capacity obtained for CA and CA^{CNT,Li} was vitiated by incomplete discharge. As the potential window in the C_{sp} formula was in the denominator and the discharge was only in half of its nominal value, the "approximated real capacity" should be divided by two. An important remark is that the very high specific surface area (786 m^2/g) recorded for carbon
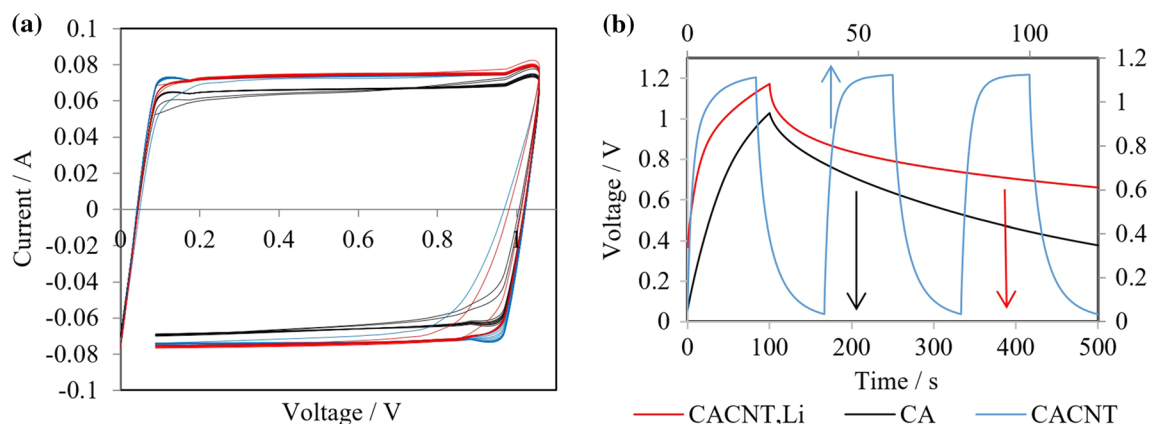
Fig. 4. CV curves (a) and charge–discharge curves (b) for carbon aerogel (black), CNT-modified carbon aerogel (blue), and CNT-modified carbon aerogel with lithium hydroxide catalyst (red) (Color figure online).

aerogel catalyzed by lithium hydroxide was an insufficient factor to enhance the specific capacity. As the gelation process is strongly dependent not only on cation species, but also on pH, the increase in pH induced by LiOH sped up gelation and produced a significant number of micropores. Mesopores with some macropores are required to satisfy proper intercalation and diffusion of electrolytes within materials. Micropores are very often too small to catch electrolyte molecules during short charge/discharge cycles. Therefore, micropores are not fully executed in solid-electrolyte layer formation. Some of electrolyte was adsorbed, but not desorbed and net specific capacity was diminished. Lithium hydroxide-catalyzed carbon aerogels modified by CNT had very small median pore width close to 0.6 nm (the covalent radius of potassium is 0.21 nm, and it is even greater for hydroxyl ions) and ca. 32% of micropores. This was a consequence of relatively poor specific capacity in comparison to material prepared using sodium carbonate. Poorer galvonastatic charge–discharge characteristic obtained for unmodified carbon aerogel resulted from the lower specific surface area (capability of solid–electrolyte layer formation).

CONCLUSIONS

It was discovered that lithium hydroxide catalyzed the process much stronger than commonly used sodium carbonate. The resulting carbon aerogel had significantly enhanced specific surface area. However, it was also found that shorter gelation time in case of lithium hydroxide catalyst completely changed pore size distribution within material. This was caused by increased pH of the reaction mixture with LiOH catalyst in comparison to Na_2CO_3. Ten times more micropores (%) were produced in comparison to traditional carbon aerogel and almost four times more with respect to the CNT-modified aerogel synthesized using sodium carbonate. An increased number of micropores

were produced at the expense of mesopores, which are thought to be transportation channels for electrolytes. As-obtained material was examined with respect to energy storage applications in hybrid symmetric supercapacitors. An excess of micropores caused some part of the material not to participate in the charge/discharge mechanism. Consequently, the specific capacitance was lower than for typical sodium carbonate-catalyzed carbon aerogel and for the same material with CNT added. The idea to prevent from too many micropores formation is to shorten gelation time from 7 days to up to 5 days to limit material shrinkage. This probably may produce material with large specific surface area and appropriate pore size distribution.

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