Pseudocapacitive Behavior of Carbon Nanoparticles Modified by Phosphomolybdate Acid

Sunjin Park,a,* Keryn Lian,a,*** and Yury Gogotsib,***

*Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario M5S 3E4, Canada
**A.J. Drexel Nanotechnology Institute and Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania 19104, USA

Chemically modified carbon nanomaterials, such as nanodiamond (ND) soot, onionlike carbon (OLC), and carbon nanotubes (CNTs), were investigated as electrodes for electrochemical capacitors in high rate applications, that is, applications that drain power very fast. A layer of Keggin-type polyphosphomolybdate (PMO12) was coated on carbons through “layer-by-layer” deposition by alternating electrostatic adsorption of cationic [i.e., poly(diallyldimethylammonium)chloride] and anionic (i.e., PMO12) species to add pseudocapacitance to improve current response and increase capacitance. This modification was successful on OLCs and CNTs but not on ND soot. This difference is due to variations in surface chemistry, structure, and sp2/sp3 content of those materials. In particular, the modified OLC exhibited a 20% increase in capacitance with up to 600 mF/cm² capacitance at 5 V/s, illustrating its high rate capability.

© 2009 The Electrochemical Society. [DOI: 10.1149/1.3223964] All rights reserved.

The electrochemical capacitor (EC) is a promising energy storage device that can provide both high power and energy, thus bridging the gap between conventional batteries and electrolytic capacitors. Current commercial ECs are electrochemical double layer capacitors (EDLCs) with high surface area electrodes that are manufactured from activated carbon materials. The widely varying particle sizes and pore structures of activated carbon result in lower electric conductivity, limiting their use in applications requiring high power. In the search for high performance yet low cost electrodes for EDLCs, nanostructured carbons with controlled nanostructures, such as carbon nanotubes (CNTs), graphene, and nanofibers, as well as nanodiamond (ND) soot and onionlike carbon (OLC), were investigated as alternative electrode materials. These materials have high electrical conductivity and a surface area comparable to activated carbon, enabling the construction of high performance, high efficiency EDLCs at relatively low cost.

ND was discovered in the 1960s in the former Soviet Union in a soot from detonation of explosives; however, extensive research of this material has not been conducted until recently. Several research groups reported that when annealed at temperatures from 1200 to 2000°C, the NDs graphitize and turn into OLC. As a result, their electrical conductivity increases significantly. The highest surface area and conductivity is obtained when ND soot is annealed at 1800°C, at which point it is completely transformed to OLC. Studies of electrochemical properties of ND soot by Portet et al. demonstrated that OLC produced at 1800°C is an optimal EDLC electrode material for high rate applications in both aqueous and nonaqueous electrolytes. The annealing of ND at higher temperatures leads to polymerization, which decreases the surface area of OLC.

Further improvement of these promising electrode materials in terms of their energy density is possible by adding pseudocapacitance through chemical modification. The pseudocapacitance is capacitance induced by an electrochemical redox reaction, which can be obtained from mixed oxides such as ruthenium oxides, polyaniline, or conducting polymers such as poly(3,4-ethylenedioxythiophene), among others. These pseudocapacitive materials are much higher in capacitance than can be achieved from an EDLC alone. Among the pseudocapacitive materials, Keggin-type PMO12, a class of transition-metal oxide clusters, was found to have fast kinetics and multiple electron transfers. It is also much cheaper than many other pseudocapacitive materials. Performance enhancement of CNT-based EDLC utilizing PMO12 surface modification was also reported. These surface modification schemes involved sonication of carbon powder materials in PMO12 solution, followed by several purification steps. Several groups showed successful modifications with PMO12 via layer-by-layer (LBL) deposition on different conducting substrates including indium tin oxide, glassy carbon, and carbon black by alternating electrostatic adsorption of cationic [i.e., poly(diallyldimethylammonium chloride (PDDA)] and anionic (i.e., POM) species, and PMO12 proves to be a much simpler and more efficient technique than other modification approaches. The ND soot and OLC have the advantage of a small (~5 to 6 nm) particle size and high specific surface area, which are easily accessible to the electrolyte. So far, the addition of pseudocapacitance on ND soot or OLC through surface modification was not investigated.

In this work, we examined the effect of the chemical modification of ND soot and OLC, produced by annealing ND soot at 1800°C, as electrode materials for EC. The objectives of this study were twofold: (i) to add pseudocapacitance to ND soot and OLC via chemical modification with a Keggin-type phosphomolybdate PMO12O40 and (ii) to understand the effect of the structure and surface chemistry of these carbon nanoparticles on their chemical modification in comparison with CNT. Cavity microelectrodes (CMEs) were employed instead of conventional mesh/film electrodes for a faster and more efficient analysis and for exploring high rate regimes that cannot be accessed using conventional cells. Surface modification via self-assembled LBL deposition was utilized.

Experimental

Materials.— Conducting ND soot (UD-50 grade) containing up to 70% of sp2 carbon was obtained from NanoBlox, Inc., and OLC was produced at Drexel University by annealing in a vacuum furnace at 1800°C, as described by Portet et al. Multiwalled carbon nanotubes (MWCNTs) were obtained from Arkema.

All materials were fabricated into a film to ensure consistent results. The ND soot and OLC films contained 4 wt % polystyrene as a binder. To manufacture the films, the binder was ultrasonically dispersed in isopropyl alcohol and mixed with carbon powder. Then, the mixture was dried in an oven at 80°C for 1 h and pressed into a film. For comparative purposes, MWCNTs were prepared in a similar manner.

All carbon materials were chemically modified using 5 M HNO3, 4 wt % PDDA, and 6 mM/L (or 6mM) phosphomolybdate acid (PMO12). All chemicals were commercially available (Aldrich) and were diluted to the desired concentration with deionized water.

Experimental

Materials.— Conducting ND soot (UD-50 grade) containing up to 70% of sp2 carbon was obtained from NanoBlox, Inc., and OLC was produced at Drexel University by annealing in a vacuum furnace at 1800°C, as described by Portet et al. Multiwalled carbon nanotubes (MWCNTs) were obtained from Arkema.

All materials were fabricated into a film to ensure consistent results. The ND soot and OLC films contained 4 wt % polystyrene as a binder. To manufacture the films, the binder was ultrasonically dispersed in isopropyl alcohol and mixed with carbon powder. Then, the mixture was dried in an oven at 80°C for 1 h and pressed into a film. For comparative purposes, MWCNTs were prepared in a similar manner.

All carbon materials were chemically modified using 5 M HNO3, 4 wt % PDDA, and 6 mM/L (or 6mM) phosphomolybdate acid (PMO12). All chemicals were commercially available (Aldrich) and were diluted to the desired concentration with deionized water.

All carbon materials were chemically modified using 5 M HNO3, 4 wt % PDDA, and 6 mM/L (or 6mM) phosphomolybdate acid (PMO12). All chemicals were commercially available (Aldrich) and were diluted to the desired concentration with deionized water.

All carbon materials were chemically modified using 5 M HNO3, 4 wt % PDDA, and 6 mM/L (or 6mM) phosphomolybdate acid (PMO12). All chemicals were commercially available (Aldrich) and were diluted to the desired concentration with deionized water.
ND soot and OLC were coated in three steps via LbL deposition in the order HNO_3, PDDA, and PMO_{12} for 2, 10, and 15 min, respectively (Fig. 1). The substrates were washed with deionized water after each coating step. All samples were coated only once.

**Electrochemical measurements.**— Cyclic voltammetry (CV) tests were conducted using a typical three-electrode cell with CME as the working electrode, Pt gauze as the counter electrode, and Ag/AgCl as the reference electrode. The construction of CME was reported in a previous paper. All experiments were carried out in a 1 M H_2SO_4 solution, and electrochemical properties were measured with a Princeton Applied Research 273A potentiostat using PowerSuite software. Capacitance was calculated by measuring the charge (Q) under the CV curves and dividing them by the tested voltage range (V).

**Material characterization.**— Scanning electron microscopy (SEM) micrographs were taken using Hitachi S-5200. X-ray diffraction (XRD) data were collected on a Siemens D5000 diffractometer with a line focus of Cu Ka source combined with a solid-state Kevex detector. X-ray photoelectron spectroscopy (XPS) was conducted using Leybold (Specs) Max 200 with a monochromatic Al Ka X-ray source. Surface chemical information was obtained in a high energy resolution mode, and all XPS spectra were calibrated at the C 1s peak at 284.6 eV.

**Results and Discussion**

ND soot and OLC are virtually micropore-free, but they possess quite different physical properties, summarized in Table I. Although originated from ND, OLC has 2 orders of magnitude, a higher electrical conductivity, and a higher surface area than ND. The OLC has a lower content of impurities, compared with as-received ND soot, due to the removal of functional groups and the evaporation of metal contaminants during heat-treatment. In our previous CV study on H_2SO_4 electrolyte, OLC was able to maintain its capacitive response under a high voltage scan rate (up to 9 V/s), superior to ND soot.14

Portet et al. reported on the electrochemical behavior of these materials in organic electrolytes for EDLC. In both studies, OLC demonstrated a much better rate response than ND, making it a good candidate for high power and fast discharge applications. In this study, we performed a chemical modification of these materials to further increase their capacitance (energy density) via the addition of the pseudocapacitance.

**Table I. Physical properties of ND soot and OLC.**

<table>
<thead>
<tr>
<th></th>
<th>ND soot (UD-50)</th>
<th>OLC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment</td>
<td>Raw detonation soot</td>
<td>Annealing ND soot at 1800°C</td>
</tr>
<tr>
<td>Structure</td>
<td>Amorphous carbon, carbon onion, fullerene shells,</td>
<td>Carbon onion</td>
</tr>
<tr>
<td></td>
<td>graphite ribbons, ash, and iron</td>
<td></td>
</tr>
<tr>
<td>Conductivity</td>
<td>0.025 S/cm</td>
<td>4 S/cm</td>
</tr>
<tr>
<td>Surface area</td>
<td>380 m^2/g</td>
<td>520 m^2/g</td>
</tr>
<tr>
<td>Particle size</td>
<td>5 nm</td>
<td>6 nm</td>
</tr>
<tr>
<td>Porosity</td>
<td>~5 vol % of micropores, d &lt; 2 nm</td>
<td></td>
</tr>
</tbody>
</table>
redox reactions with protons in the electrolyte. Upon annealing of ND, the surface defects, or edge planes, and the surface functional groups are removed, resulting in a decrease in capacitance, as explained by Portet et al. The opposite effect was observed when chemically modifying ND soot and OLC with PMo$_{12}$ because the capacitance comes from PMo$_{12}$ in that case, while carbon provides the surface area and a conductive network. After coating with one layer of PMo$_{12}$, the current density significantly decreased on ND but increased on OLC. As depicted in Fig. 2a, ND soot lost its characteristic peaks and became more resistive, showing a skewed CV profile. OLC showed a significant increase in current with very small oxidation/reduction peaks hinting at the presence of PMo$_{12}$/H$_2$O.

Although these oxidation/redox peaks were small, they can still be related to molybdenum reduction/oxidation I and II at around 0.35 and 0.2 V and oxidation/reduction I' and II' at around 0.45 and 0.3 V). The proposed successive two-electron transfer sequence is as follows:

$$\text{PMo}_{12}^{4+} + 2e^- + 2H^+ \rightleftharpoons H_2\text{PMo}_{8}^{6+}$$

$$H_2\text{PMo}_{8}^{6+} + 2e^- + 2H^+ \rightleftharpoons H_4\text{PMo}_{4}^{8+}$$

Surface analysis.— To understand the reasons for the difference in the results of PMo$_{12}$ modification on ND soot and OLC, we conducted morphological, structural, and surface analyses of these materials. The surface morphologies of ND soot and OLC films before and after chemical modification were examined using SEM (Fig. 3). Before PMo$_{12}$ modification, both ND soot and OLC had similar morphologies with fairly uniform dispersion of nanosized particles (Fig. 3a and c). After the modification, however, the morphologies of ND soot and OLC were rather different. The film morphology of the modified ND soot did not show a significant change from the bare ND soot (Fig. 3b), whereas a netlike structure was obtained for OLC (Fig. 3d). The difference in morphologies is indirectly supportive of the results found in CV, which electrochemically demonstrated the effect of coating on OLC. Further in-depth analysis is necessary to identify the root cause of this difference between ND soot and OLC.

XRD and XPS were employed to study the crystal structure and surface chemistry of bare ND soot and OLC. Figure 4 shows the spectra of XRD for both ND soot and OLC. Both materials have relatively broad peak widths due to the small particle size. As XRD reveals, ND soot is comprised of a mixture of diamond, graphite, and some mineral impurities such as iron oxide (magnetite), while OLC is mainly graphite (Fig. 4). The XRD results agree with those reported in the literature showing transitions of ND to OLC (mostly graphite) upon annealing. We would expect these differences to influence bonding of these nanocarbons to external molecules such as, in this case, PMo$_{12}$.

Figure 4. XRD spectra of bare ND soot and bare OLC.

Figure 3. SEM images of (a) bare ND soot, (b) PMo$_{12}$-modified ND soot, (c) bare OLC, and (d) PMo$_{12}$-modified OLC.

$$\text{PMo}_{12}^{4+} + 2e^- + 2H^+ \rightleftharpoons H_2\text{PMo}_{8}^{6+}$$

$$H_2\text{PMo}_{8}^{6+} + 2e^- + 2H^+ \rightleftharpoons H_4\text{PMo}_{4}^{8+}$$

$$\text{PMo}_{12}^{4+} + 2e^- + 2H^+ \rightleftharpoons H_2\text{PMo}_{8}^{6+}$$

$$H_2\text{PMo}_{8}^{6+} + 2e^- + 2H^+ \rightleftharpoons H_4\text{PMo}_{4}^{8+}$$

[1]
By estimating the area of deconvoluted XPS peaks (Fig. 5), the ratio of sp\textsuperscript{2}/sp\textsuperscript{3} was 1.1 for ND soot and 11.4 for OLC, indicating a significant increase in the transition from a diamond to a graphite structure upon annealing.

Analyses on PMO\textsubscript{12}-modified ND soot and OLC provided additional information that supported this notion. Figure 6 shows XPS broad scans on (i) PMO\textsubscript{12}-coated ND soot and (ii) OLC. In Fig. 6, we can see the presence of Mo, in addition to C and O. Quantified elemental compositions (in atom % and wt %) for bare and PMO\textsubscript{12}-coated ND soot and OLC are listed in Table III. Phosphorus was not included due to its very low content (\(-0.35\) to 0.75 atom %).

Initially, ND soot and OLC surfaces consisted of 93–95 wt % carbon and 5–7 wt % oxygen. After PMO\textsubscript{12} modification, the carbon content on the OLC surface decreased to 35 wt %, while the carbon content on the ND soot surface was 59 wt %.

The different surface coverages of Mo and O on ND soot and OLC agree with the observations in Fig. 3, where PMO\textsubscript{12} coating on ND soot was sparse, while PMO\textsubscript{12}-coated OLC showed a continuous “netlike” morphology. Considering the atom % of Mo and O in Table III, we can see that the coating preserved the molybdenum-to-oxygen ratio in the PMO\textsubscript{12} molecule, PMO\textsubscript{12}O\textsubscript{40}, which suggests that the deposited PMO\textsubscript{12} retained its Keggin-type structure. The XPS results may also be used to explain the small characteristic peaks in Fig. 2b. Because the modification was merely one coat with 65% coverage, we would expect more distinguished redox peaks with a thicker multilayer coating.

The difference in the electrochemical behavior and surface morphology of PMO\textsubscript{12}-coated ND soot and OLC can be attributed mainly to the differences in their sp\textsuperscript{2} and sp\textsuperscript{3} contents. The sp\textsuperscript{3} bonds are saturated bonds, which are more inert than unsaturated bonds such as sp\textsuperscript{2}. The latter would facilitate the LbL coating with improved continuity and connectivity between the particles.

In ND, the surface was a mixture of sp\textsuperscript{3} and sp\textsuperscript{2} together with other species. For ND, the addition of PMO\textsubscript{12} had an adverse effect...
on the conductivity and capacity of this resistive material (Table I). For one, the surface may have only been partially covered by PMO$_{12}$ molecules due to discontinuous and sparse deposition, as seen in the SEM (Fig. 3b). The poor quality coating may have also covered other surface functional groups and diminished the characteristic peaks of ND soot in the CV, resulting in reduced current and capacitance (Fig. 2a).

In contrast, OLC, dominated by a graphitic sp$^2$ structure, facilitated the formation of a more continuous and locally connected network of PMO$_{12}$ molecules on the surface (Fig. 3d). The increase in current response after coating is likely due to pseudocapacitive redox reactions of PMO$_{12}$ and enhanced proton conductivity at the electrode surface through hydrophilic PMO$_{12}$O$_{40}^{2-}$ anions (Fig. 2b). Therefore, we suggest that the surface structure and chemistry, along with the sp$^2$/sp$^3$ ratio, is responsible for the difference in behavior after surface coating of ND soot and OLC. A higher sp$^2$/sp$^3$ ratio is desirable for chemical modification of carbon materials including the carbon nanoparticles.

Confirmation test.—To further verify the role of sp$^2$ carbon in surface modification with PMO$_{12}$, a separate confirmation experiment with MWCNT was conducted. Figure 7 depicts the CV profiles of MWCNT before and after modification. MWCNT was successfully modified with PMO$_{12}$ displaying even more defined Mo redox peaks compared to that of OLC, even though the overall capacitance of modified MWCNT was still lower than that of both bare and modified OLC. The result shown in Fig. 7 supports the notion of sp$^2$ easing the coating of PMO$_{12}$. The fact that modified MWCNT displayed an even greater increase in capacitance and a clear signature of PMO$_{12}$ oxidation/reduction may be related to the differences in active coating sites available on these materials. For MWCNT, surface functional groups or reactive sites are predominantly available at edge plane or edge-plane-like defect sites, whereas for OLC, most of the surface defects were removed upon annealing and have closed fullerene-like shells resulting in mostly basal-like planes.

High rate response.—A detailed analysis of MWCNT is beyond the scope of this paper. However, as shown in Fig. 8, the PMO$_{12}$-coated OLC delivers the highest energy (possesses the highest capacitance) at high rates (>0.5 V/s) among all the nanomaterials studied, including CNT. Although bare ND soot has a larger capacitance than bare OLC at low scan rates (50–200 mV/s), its capacitance diminishes rapidly as the scan rate increases, similar to the behavior of activated carbon due to its relatively low conductivity. The same behavior was also observed for bare ND and OLC studied in organic electrolyte. After modification, the capacitance of ND soot decreased even more drastically with the scan rate, reflecting the negative effect of PMO$_{12}$ coating, which further decreased the conductivity of the electrode. Beyond 1 V/s, the CV of both bare and coated ND soot electrodes were so distorted and resistive that the capacitance became difficult to extract. In contrast, OLC could sustain its capacitance beyond 1 V/s and showed about a 20% increase in capacitance after PMO$_{12}$ coating on average. Chemically modified OLC has up to 600 mF/cm$^2$ capacitance at 5 V/s. Compared to its capacitance at a low rate (50 mV/s), PMO$_{12}$-modified OLC can deliver 87% of the charge at a rate of 1 V/s, while ND soot can deliver only about 50% of the stored charge. This result is very encouraging for OLC materials and suggests a continued investigation of the surface modification of these materials for high rate applications, especially in thin film devices for electrical energy storage that can provide higher power compared to lithium ion and other batteries.

Conclusion

Surface modification with PMO$_{12}$ increased the capacitance of OLC with only a single coat. A “locally connected network” structure formed in OLC, which enhanced the conductivity and connectivity between the particles and the coated PMO$_{12}$ sites. Through modification, the capacitance of OLC increased by 20%, on average, exhibiting up to 600 mF/cm$^2$ capacitance at 5 V/s. The modification of ND soot, however, had a detrimental effect and drastically decreased its capacitance. This divergence was attributed to differences in the surface structure, as well as in the sp$^2$ and sp$^3$ contents of ND soot and OLC, which led to large differences in their conductivity. A confirmation test was carried out with MWCNT, which further supported the notion that a highly graphitic surface enables PMO$_{12}$ modification to increase capacitance. Based on these results, chemically modified OLC is probably most suitable for high rate/high power applications.

Acknowledgment

We thank NanoBlox, Inc. for generously providing ND soot, Arkema for MWCNT samples, Dr. C. Portet for OLC synthesis, Dr. R. Sodhi and P. Brodersen from SI Ontario for XPS, Dr. Sr. Petrov from PXRD Analysis Laboratory for XRD, Natural Sciences and Engineering Research Council of Canada, and U of T Open Fellowship for financial support.

University of Toronto assisted in meeting the publication costs of this article.

References

A926
