

Facile Conversion of the Surface Layers of Graphite to Capacitive Manganese Oxide Coatings

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A simple method to convert graphite to manganese oxide coatings is presented in this paper. The as-grown coatings were characterized by X-ray photoelectron spectroscopy, X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray analyses, and thus verified to be largely amorphous manganese oxide. The coatings behave typically capacitive in various neutral aqueous solutions of alkali metal salts, e.g., 0.5 M LiCl, 0.5 M NaCl, and 0.5 M KCl. The capacitance per geometric electrode surface area ( $C_a$ ) from cyclic voltammetry in 0.5 M NaCl increased to 67.2 mF/cm<sup>2</sup> when the conversion time was up to 120 min, obeying the logarithm law very well. In addition, the capacitance per mass of the coating ( $C_m$ ) of 362, 385, 380, and 374 F g<sup>-1</sup> was achieved with the manganese coatings grown for 10, 30, 60, and 120 min, respectively. Electrochemical measurements demonstrated evident differences in capacitive behaviors of the coatings in the three above-mentioned electrolyte solutions. It was confirmed that this facile conversion of the surface layers of graphite offers a simple and efficient formation of thin-film super-capacitors promising for industrial applications.

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In recent decades, much attention has been focused on electrochemical supercapacitors based on pseudocapacitance from faradaic redox reactions. Accordingly, there have been increasing attempts to develop cost-effective pseudocapacitive materials instead of the pre-cious metal ruthenium oxides,<sup>1,2</sup> such as nonprecious metal oxides<sup>3-9</sup> and nitrides,<sup>10-12</sup> composites.<sup>15-17</sup> electroactive polymers,<sup>13,14</sup> and their Amorphous hydrous manganese oxides (a-MnO<sub>2</sub>·nH<sub>2</sub>O) recently have been attracting considerable interest as the most promising electrode materials. Most of the efforts are focused on depositing a-MnO\_2  $\cdot nH_2O$  thin films onto the electron collectors. In a universally used sol-gel technique, the formation of a hydrous MnO<sub>2</sub> coating is achieved by a process involving the reduction of the permanganate anion  $(MnO_4^-)$  with a mild reducing agent such as  $Mn^{2+}$ .

In addition, an anodic electrochemical deposition of  $a-MnO_2 \cdot nH_2O$  was extensively reported, but the obtained materials had not yet achieved a particularly high specific capacitance.<sup>21-26</sup> More encouragingly, the potentiodynamically deposited amorphous nanostructured form of hydrous  $MnO_2$  was found to achieve a specific capacitance of 482 F/g.<sup>27</sup> Successively, microporous, amorphous nickel–manganese oxides and cobalt–manganese oxides were also deposited at high scan rates with specific capacitance as high as 621 and 498 F/g.<sup>28</sup> respectively. Despite this, a specific capacitance of only 125 F/g was achieved by Chuang and Hu<sup>29</sup> for the anodically deposited hydrous manganese–cobalt oxides [(Mn,Co)Ox·nH<sub>2</sub>O]. Undoubtedly, the electrochemical capacitance is dependent on the film-depositing conditions. It was also reported that an electrochemical oxidation of a Mn/MnO film in a 1 M Na<sub>2</sub>SO<sub>4</sub> solution can cause the formation of an electrochemical capacitance, and the porous surface layer is likely responsible for the capacitive tendencies of the films<sup>30</sup>.

In the preliminary work,<sup>31</sup> a one-step controllable redox deposition method was briefly described, which was developed from the viewpoint of the surface modification of a graphite electrode with oxidative potassium permanganate (KMnO<sub>4</sub>) in an acidic aqueous solution at room temperature. Most recently, several researches<sup>32,37</sup> employed this simple route to fabricate structured MnO<sub>2</sub>–carbon composites mainly for electrochemical supercapacitors. In the present work, the surface layers of graphite disk electrodes were converted to manganese oxide coatings in an acidic KMnO<sub>4</sub> solution bath at 50°C, and the capacitive performances of the as-grown coatings were investigated comprehensively. The aim of this work is to confirm that this facile conversion of the surface layers of graphite facilitates the simple and efficient formation of promising thin-film supercapacitors economical for industrial applications.

# Experimental

Graphite disk electrodes were prepared in a procedure described in detail elsewhere.<sup>31</sup> The as-fabricated graphite electrodes were placed vertically in a bath containing freshly prepared 0.25 M KMnO<sub>4</sub> in a solution of 0.5 M H<sub>2</sub>SO<sub>4</sub>, which was continuously stirred during the conversion. The conversions were carried out at 50°C in the identical but fresh solutions for the desired time durations. Upon conversions, the coatings were well rinsed with distilled water, cleaned ultrasonically for 30 min, and dried by a flow of cool air. The scanning electron microscopic (SEM) images were recorded with a JSM-5800LV microscope (JEOL, Japan), and the energydispersive X-ray analyses (EDX) data were collected simultaneously. The X-ray diffraction (XRD) measurements were performed on an X-ray diffractometer (X'PertProMPD, Philips Co.) using Cu Ka radiation, and X-ray photoelectron spectroscopy (XPS) analysis was carried out on an XSAM 800 spectrometer equipped with a Mg K $\alpha$  radiation. The mass of the grown manganese oxide films was determined by flame atomic absorption spectrometry. First, a manganese oxide film was thoroughly converted to a manganese ionic solution of sample by treatment with 1.0 mol L<sup>-1</sup> nitric acid. An AA 6800 atomic absorption spectrometer (Shimadzu, Japan) was utilized for the manganese measurements. A manganese hollow cathode lamp operating at 6 mA was used as the radiation source. The primary resonance line at 279.5 nm was applied with a bandwidth of 0.5 nm. The acetylene flow rate and the burner height were adjusted for a maximum absorbance signal by aspirating a solution of the sample.

The coatings were comprehensively evaluated via cyclic voltammetry (CV), chronopotentiometric (CP), and electrochemical impedance spectroscopy (EIS) with a CHI760B computer-controlled electrochemical workstation. An alternate current (ac) potential amplitude of 10 mV was employed for the impedance measurements in the frequency range between 100 kHz and 0.1 Hz. All electrochemical measurements were conducted at room temperature in a beaker-type electrochemical cell equipped with a coating-covered graphite working electrode, a Pt wire counter electrode, and a Ag/ AgCl (3 M KCl) reference electrode. Various neutral aqueous electrolyte solutions of alkali metal salts were utilized in the electro-

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Figure 1. The XPS spectra for the coating formed by conversion in 0.25 M KMnO<sub>4</sub> + 1.0 M H<sub>2</sub>SO<sub>4</sub> at 50°C for 30 min. (a) Spectrum at Mn  $2p^{1/2}$  and Mn  $2p^{3/2}$ , (b) spectrum at O 1s.

chemical characterizations, including 0.5 M LiCl, 0.5 M NaCl, and 0.5 M KCl. The specific capacitance was estimated on the basis of the following equation: C = i/(dV/dt), where *i* is the current response of the corresponding CV plot, and dV/dt is the potential sweep rate.

## **Results and Discussion**

Micrographs of the as-formed coatings after 30 min conversion were collected (not shown here). As verified in the previous work,<sup>2</sup> the coating is densely and uniformly grown onto the surface of the graphite electrode. No significant morphology difference was found between the coatings grown at room temperature and at 50°C. However, growth at high temperature was accelerated observably. To characterize the as-formed coatings, XPS and XRD analyses were conducted and the results are shown in Fig. 1 and 2, respectively. As shown in Fig. 1a, the Mn  $2p^{3/2}$  peak is centered at 642.5 eV and the Mn  $2p^{1/2}$  peak at 654.2 eV, with a spin-energy separation of 11.7 eV, which is in accordance with that reported in  $MnO_2$ .<sup>38</sup> It has also been reported that the binding energies of the Mn  $2p^{3/2}$  electron for  $Mn^{3+}$  and  $Mn^{4+}$  are 641.6 and 642.6 eV,<sup>39</sup> respectively. In addition, no clear Mn  $2p^{3/2}$  signal of KMnO<sub>4</sub> at 647 eV can be observed, confirming that the permanganate ions have been reduced to manganese dioxide by the carbon in graphite. As shown in Fig. 1b, the O 1s spectra of the coatings could be fitted into two main constituents



Figure 2. The XRD pattern for the coating formed by conversion in 0.25 M  $KMnO_4 + 1.0 M H_2SO_4$  at 50°C for 30 min.

corresponding to different oxygen-containing species such as Mn-O–H at 530 eV,<sup>40</sup> and Mn–O–H at 532 eV.<sup>41</sup> According to the areas of the XPS peaks, the atomic ratio of manganese to oxygen can be estimated to be 1: 2.12, which is in agreement with that suggested by the EDX analysis (not shown here). Besides the sharp diffraction peak at 26° associated with the graphite, the peaks at around 38, 56, and 68° show a certain degree of fine crystalline structure, which should be attributed to peaks (211), (600), and (002) of  $\alpha$ -MnO<sub>2</sub>, respectively. Nevertheless, the XRD pattern generally has a lack of clear peaks, and a wide broadening, indicating the amorphous nature of the coating. Without further heat treatment, the as-formed coating is thus presumably amorphous manganese oxide. Actually, to purify and open carbon nanotubes in high yield,  $KMnO_4$  has been considered to be the best oxidant in an acidic solution.<sup>42</sup> It was also demonstrated that permanganate was transferred to manganese (IV) oxide as a by-product, but washed off. However, the evolution of  $CO_2$ gas was not noticed during the period of electrode immersion in this work. This is very likely attributed to the continuous stirring having removed the gaseous products before it formed a visible bubble on the electrode surface. Nevertheless, a vigorous bubbling did occur when adding graphite powder into an identical conversion solution, which is in accordance with Reaction 1

$$4KMnO_4 + 3C + 2H_2SO_4 \rightarrow 4MnO_2 + 3CO_2 + 2K_2SO_4 + H_2O$$
[1]

Actually, Kim et al.<sup>32</sup> clarified this reaction process in the system of acetylene black and acidic KMnO<sub>4</sub> solution via an in situ monitoring of the reduction potential and pH of the solution and supplementary ultraviolet-visible analysis. Because there likely exists a less complete oxidation of carbon, as was demonstrated by Zoval et al.<sup>43</sup> for the formation of platinum particles on highly oriented pyrolytic graphite, no attempt was made to estimate how much grew onto the surface of the graphite by weighing the electrode before and after the conversion process. But, basically, the mass of a coating can be controlled by employing a different conversion time, and should increase with the conversion time.

Typical CVs measured in a 0.5 M NaCl aqueous solution for the coatings formed by different conversion time are shown in Fig. 3. These CVs clearly exhibit the rectangular and symmetric current-potential characteristics of a capacitor, except at potentials near the two limits of the potential window. Additionally, even at a high potential scan rate of 1000 mV/s, the CVs were found to still show a capacitive-like behavior, i.e., a rectangular-like shape. More significantly, the voltammetric current response and thereby the capacitance of the coating increase substantially with the conversion time. As shown in Fig. 4, the capacitance per geometric electrode surface



Figure 3. Cyclic voltammograms, measured in 0.5 M NaCl at 10 mV/s, of the coatings formed by different time durations.

area ( $C_a$ ), derived from the CV currents, increases to 67.2 mF/cm<sup>2</sup> with the conversion time, up to 120 min, following the logarithm law very well. Undoubtedly, the increase in capacitance is due to the increase in Mn sites of the MnO<sub>2</sub> coatings. Presumably, the logarithm law could be ascribed to the diffusion process involved in the conversion reactions. The data presented in Fig. 4 are averaged values over four scan rates, i.e., 5, 10, 25, and 50 mV/s. The capacitance is significantly larger than that previously reported for the  $\frac{31}{31}$ coating grown at room temperature for the same conversion time. The logarithm law is as well expected to imply the dependence of deposit mass or deposit thickness on the conversion time. As expected, no sharp interface was observed between the coating and the graphite substrate, and the deposit thickness is not easily determined at the observation of cross-section SEM imaging and EDX analysis. Actually, these observations also confirm the origin of the MnO<sub>2</sub> coating from the graphite substrate itself. Although admittedly it is quite understandable, an attempt to make careful EDX analyses should be encouraged and helpful to probe the interface between the coating and the graphite substrate. Although the maximum specific capacitance for the utmost long conversion time has not been reached in this work, further improvements could be anticipated by the above-mentioned logarithm law. The linear relationship between the reaction extent and the logarithm of conversion time does hold



Figure 4. The logarithm relationship between the specific capacitance  $(C_a)$  and the conversion time.



Figure 5. The comparison of the voltammetric current of the coatings formed by 10 and 60 min in three neutral aqueous solutions.

in this specific range. No attempt was therefore made to pursue the maximum. For the sake of comparison between our results and those in the literature, the capacitance per mass of the coating ( $C_m$ ) was also calculated with the mass evaluated using atomic absorption spectroscopy. The average specific capacitances of 362, 385, 380, and 374 F g<sup>-1</sup> in a 0.5 M NaCl aqueous solution were achieved from CV with the manganese coatings grown for 10, 30, 60, and 120 min, respectively. The results seem a little less than that with the potentiodynamically deposited nanostructured manganese dioxide films by Miura et al.,<sup>27,44</sup> specifically, a maximum capacitance of 410–482 F g<sup>-1</sup> at a scan rate of 10 mV s<sup>-1</sup>. It is, however, higher than that with the anodically deposited hydrous manganese oxide films by Hu et al.,<sup>21</sup> i.e., 265–320 F g<sup>-1</sup>.

The applicability of different neutral electrolytes for manganese oxide-based electrode materials in supercapacitors has been investigated.<sup>19,20,45</sup> It was found that amorphous or crystallite manganese oxide could be effectively used in several neutral electrolytes, and it was thus helpful for practical application and storage safety. Figure 5 compares the voltammetric current responses of the coatings formed by 10 and 60 min in three neutral aqueous solutions. In order not to cause a significant difference in the electrical resistance and alkali metal ionic concentration of the electrolyte, 0.5 M LiCl, 0.5 M NaCl, and 0.5 M KCl were employed in the electrochemical measurements. As shown in Fig. 5, a perceptible voltammetric current difference among the three different electrolytes is well demonstrated for coatings formed by both 10 and 60 min, indicating a clear similar trend for the two coatings that the voltammetric current is increasing with decreasing the size of the cation.

To further confirm the cation influence on the capacitive properties of the grown manganese oxide coatings, Fig. 6 compares the charge–discharge plots of the coating formed by 10 min in different electrolyte solutions at the same current density of 0.885 mA/cm<sup>2</sup>, experimentally a current of 0.25 mA against the fixed graphite electrode area. The anodic charging segments, in general, are symmetric to their corresponding cathodic discharging counterparts for all three plots, indicating a high reversibility of a typical capacitive material in the three aqueous electrolyte solutions within the applied potential window, in accordance with the CV observations. The average specific capacitance of an electrode in a given electrolyte solution thus can be calculated via an equation as follows

$$C = \frac{i\Delta t}{s\Delta V}$$
[2]

where *i* is the discharge current for the applied time duration  $\Delta t$ ,  $\Delta V$  is the potential window, and *s* is the fixed graphite electrode area. Clearly, the charge–discharge plots in Fig. 6 indicate the difference



Figure 6. The charge–discharge plots of the coating formed by 10 min in different electrolyte solutions at a current density of  $0.885 \text{ mA/cm}^2$ .

of the values of  $\Delta t$  with the different employed electrolytes, and thereby reveal the dependence of the specific capacitance on the metal ion nature of electrolyte, which is in accordance with the CV measurements shown in Fig. 5. In order to explain this, one should first understand the charge storage mechanism of manganese oxide electrode used in neutral aqueous electrolyte solutions. Two main mechanisms were proposed to explain the manganese oxide charge storage. The first suggests the intercalation of protons or alkali metal cations in the bulk of the material upon reduction, followed by deintercalation upon oxidation.<sup>18</sup> The second is based on the surface adsorption of alkali metal cations on manganese oxide.<sup>6</sup> Recently, a combination of the two explanations was made to get a better understanding of the charge storage mechanism in manganese oxide electrodes.<sup>46</sup> Most importantly, protons and alkali metal cations from the electrolyte are confirmed to be involved simultaneously in the charge storage process of manganese oxide thin-film electrodes, and alkali metal cations are anticipated for charge compensation, with an implication of alkali metal cations playing an important role in the charge-discharge electrochemistry of manganese oxides. Thermodynamically, the smaller alkali metal cation may get more involved in charge compensation during the charge-discharge process, causing high capacitance. This is in agreement with Lee and Goodenough,<sup>o</sup> who claimed that the larger potassium ion appears to limit the capacity to chemisorption, and thus lowers the capacity to about one-third that with a proton.

Because the capability to discharge at a high rate is of great concern for an electroactive material of supercapacitors, the chargedischarge behavior of all the coatings grown in this work was also examined at different current densities. Figure 7 presents the specific capacitance of the coating formed by 10 min in the three abovementioned different electrolyte solutions as a function of the discharge current density. The specific capacitances in all three electrolytes decrease gradually with increasing the discharge current density. In contrast, the decrease in a 0.5 M LiCl solution is the largest, but that in a 0.5 M KCl solution is the smallest. The specific capacitance in a 0.5 M LiCl solution at a discharge current density of 17.7 mA/cm<sup>2</sup> drops by about 31.5% from that at 0.885 mA/cm<sup>2</sup>, while the specific capacitance in a 0.5 M NaCl solution drops by about 26.8%, and only 22.9% for that in a 0.5 M KCl solution. The comparatively rapid deterioration of the specific capacitance in a 0.5 M LiCl solution may be attributed to the larger internal resistance of the coating. One possible explanation is that the ion diffusion is not able to reach all the available active sites in the coating, thereby restricting the amount of material that can contribute to the measured capacitance. Dynamically, the ion diffusion resistance from hydrated cations leads to a large ohmic drop at a high discharge



Figure 7. Specific capacitance of the coating formed by 10 min in different electrolyte solutions as a function of discharge current density.

current density, thus causing the rapid decrease of the specific capacitance. Moreover, the larger size of the hydrated cation causes a higher ion diffusion resistance, and accordingly leads to a more rapid decrease in the specific capacitance with increasing the discharge current density. The ion diffusion resistance impact was therefore emphasized by the high discharge current density that makes the system far from equilibrium and highlights the kinetic behaviors of the coatings, particularly thick ones. Further supportive evidence for this hypothesis of ion diffusion resistance impact was obtained when EIS of the same coating was recorded in different electrolyte solutions. The small sine-wave amplitude (10 mV) and broad frequency range  $(10^5-0.1 \text{ Hz})$  used for the EIS measurements makes it possible to separate and study electrochemical processes having different time constants, such as electrical conduction, ion transfer, and capacitance. It can be seen that the EIS plots, shown in Fig. 8, are similar in form, and can be divided into a high-frequency component (inclined at 45°) and a low-frequency component (near vertical). The intercepts of the plots with the real impedance axis (Z') presents the uncompensated electrical resistance  $(R_{\Omega})$  of the coatings  $(R_a)$ , the electrolyte  $(R_e)$ , and the electrical leads combined  $(R_1)$ .<sup>47</sup> The (almost) same intercepts of the plots suggest negligible differences in electrical resistance of the electrolyte because the



Figure 8. Impedance Nyquist plots of the coating formed by 10 min in different electrolyte solutions.



Figure 9. Cyclic voltammograms of different cycles of the coating formed by 30 min, recorded in 0.5 M NaCl and at 100 mV/s.

electrical resistances of the leads and the coatings are the same for the three cases. More importantly, the projected length of the highfrequency Warburg line on the real axis (Z') characterizes the slow ion migration process and is equal to one-third of the coating's ionic diffusion resistance.<sup>48</sup> The EIS plots shown in Fig. 8 indicate almost the same uncompensated electrical resistances, but significant differences in ionic diffusion resistances for three different electrolytes. The coating has ionic resistances of 16.0, 24.0, and 29.5  $\Omega$  for 0.5 M KCl, 0.5 M NaCl, and 0.5 M LiCl, respectively. Although Li<sup>+</sup> is of the smallest size among the three cations, hydrated Li<sup>+</sup> is the biggest while hydrated K<sup>+</sup> is really the smallest, which just explains the lower barrier to ionic transport for the smaller hydrated ion, and a reduced kinetic difficulty for charge transfer-transport in the electrode. The low-frequency capacitance  $(C_{lf})$  of each coating was determined from the slope of a plot of the imaginary component of impedance (-Z') at low frequency, vs the inverse of frequency (f) via the equation<sup>49</sup>  $C_{\rm lf} = [-Z''(2\pi f)]^{-1}$ . The specific capacitances of the coatings formed by 10 min are thereby 36.2, 37.7, and 38.3 mF/cm<sup>2</sup> for 0.5 M KCl, 0.5 M NaCl, and 0.5 M LiCl solutions, respectively, in agreement with the measurements by CV and CP.

The long-term operation stability of an electroactive material is of great importance; the potential cycling on the coatings was thus performed in 0.5 M NaCl solution within the potential window of  $\sim 0$  to 1 V. The CVs of different cycles of the coating formed by 30 min are superimposed in Fig. 9. It is evident that there are only minor changes between the CVs, and the total areas/charges enclosed by the curves, respectively, are very much the same, suggesting the high electrochemical stability of the coating. Surprisingly, SEM observations of the coating before and after the potential cycling, however, demonstrated that the appearance visible on the initial coating became as much changed as characterized by the crosslinked needlelike substances, shown in Fig. 10. The pores between the nanoneedles are found to be approximately  $\sim 100$  to 300 nm in diameter. More encouragingly, these similar nanostructures of manganese oxides are thought to be beneficial to ionic charge transport within the coating.<sup>24,27</sup> The unchanged mass could be the graphite left in the coating. Actually, it can be further argued that the coatings formed by more than 30 min did not show an evident resistance difference in the EIS examinations. The presence of the remaining graphite within the coating makes it less compact, more conductive, and more easily attached to the graphite electrode than the anodically deposited films.

In order to prove the universal effectiveness of the as-presented facile conversion of the surface layers of graphite to capacitive MnO<sub>2</sub>, various powdery carbon materials, including graphite, car-



Figure 10. SEM image of the coating formed by 30 min imaged after 1000 potential cycles in 0.5 M NaCl.

bon black, active carbon, and carbon nanotubes, were further employed to form  $MnO_2$ -coated carbon composites for supercapacitors, which will be reported elsewhere later.

#### Conclusions

This paper presents a simple method for converting the surface layers to manganese oxide coatings for thin-film supercapacitor applications, which is simply immersing the graphite electrodes in an acidic aqueous solution of potassium permanganate at 50°C for given time durations. In neutral aqueous solutions of the alkali metal salts, including 0.5 M LiCl, 0.5 M NaCl, and 0.5 M KCl, the asformed coatings exhibit quite a satisfactory capacitance that is very much comparable to that prepared by the more widely used anodic deposition method. The specific capacitance of the coatings from CV in a 0.5 M NaCl solution increases to 67.2 mF/cm<sup>2</sup>, following very well the logarithm law with the conversion time. In addition, the average specific capacitances of 362, 385, 380, and 374 F  $g^$ were achieved with the manganese coatings grown for 10, 30, 60, and 120 min, respectively. The CV, CP, and EIS analyses confirmed the differences in capacitive behaviors of the coatings in the above three neutral aqueous solutions. Continuous cycling of the potential upon a manganese oxide-coated graphite electrode up to 1000 cycles caused very little change in the capacitance. SEM observation, however, confirms morphology changes at the nanometer scales. It was confirmed that this facile conversion of the surface layers of graphite offered a simple and efficient formation of thin-film supercapacitors economically promising for industrial applications.

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