High-performance carbon-based supercapacitors using Al current-collector with conformal carbon coating

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Abstract

Al current-collector with porous surface is coated with a conformal carbon (C) layer via a chemical vapor deposition process in CH₄ at 600 °C. X-ray photoelectron spectroscopy analysis indicates that the coating process leads to the replacement of native aluminum oxide with a composite coating consisting of an Al₄C₃ interfacial layer and a C top layer. Activated C-based supercapacitors employing the resulting C-coated Al current-collectors have exhibited remarkably enhanced high-rate performance, and the enhancement can be attributed to two accounts. Firstly, the current-collector/active-layer interface resistance is reduced due to removal of the insulating oxide layer and improved adhesion of the active-layer on the current-collector. Secondly, the presence of the conducting C layer shortens the effective current conduction distance from the solid-electrolyte interface to the current-collector, leading to reduced charge-transfer resistance within the active-layer. Combining the C-coated Al current-collector with a C fiber active-layer that contains a large mesoporous pore volume (0.4 cm³ g⁻¹) has resulted in high-performance supercapacitors that exhibit, for instance, a cell specific energy of 18 Wh Kg⁻¹ at 25 °C or 7 Wh Kg⁻¹ at −10 °C under a cell specific power of 25 KW Kg⁻¹.

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1. Introduction

Supercapacitor, also known as electrochemical capacitor, is an electrochemical energy storage device designed to give high-power charge/discharge capability. Although there are various types of supercapacitors employing different electrode materials [1–6], the activated carbon (C)-based supercapacitor remains the most widely studied technology. This class of supercapacitor typically contains two identical electrodes of which each consists of an active-layer of activated C particles on an Al current-collector. Charge storage proceeds mainly via reversible adsorption of ions at the C-electrolyte interface. The activated C particles are highly porous and provide high (mostly > 1000 m² g⁻¹) specific surface areas for sufficient energy storage.

The high-power capability of a supercapacitor (and other electrochemical devices as well) is basically represented by the amount of energy delivered (or stored) under high current rates. The basic principle for achieving high-power capability is minimizing the overall resistance of the electrochemical system, which would otherwise cause energy loss during charge/discharge. In the case of activated C electrodes described above, there are three major resistance sources, including (1) the ionic resistance associated with diffusion of electrolyte ions within the pores of C particles, (2) the electronic resistance within the framework of active-layer, and (3) the electronic resistance at the interface between current-collector and active-layer. The bulk electronic resistance of Al current collect is typically negligible.

Earlier studies [e.g., 2, 7-9] on supercapacitor power performance have focused mainly on the pore structures of constituent C materials, which govern the ionic resistance. They in general suggested the beneficial effects by mesoporosity, in contrast to microporosity, of the C materials on facilitating diffusion of electrolyte ions without sacrifice of specific surface area. However, recent studies [10,11] showed anomalous increase in specific capacitance within micropores with pore size less than 1 nm. In addition, introducing sufficient amount of conductive additive to exceed percolation threshold has been shown to be critical to the reduction of electronic resistance of active-layer in some occasions [12].

Recent publications by Simon et al. [13–15] have drawn attention to the importance of the electric resistance at the interface between Al current-collector and C active-layer. In their work, etched Al current-collector was coated with a polymeric film containing carbonaceous particles, which was subsequently pyrolyzed. The resulting supercapacitors showed significantly reduced interfa-
cial resistance. The chemical and microstructural properties of the C coating were, however, not revealed.

In this work, Al current-collector with a conformal C coating has been prepared by a chemical vapor deposition (CVD) process. Combination of this current-collector with a carbon fiber active-layer that contains a large mesoporous pore volume has resulted in supercapacitors of remarkably enhanced high-rate capability. The structural and electrochemical properties of both components and the entire cell were characterized, and the interplay between these properties was investigated in order to reveal the enhancing mechanism(s) due to the C coating.

2. Experimental

2.1. Materials preparation and characterization

To prepare the C-coated current-collector, a surface-etched Al foil 4 cm × 10 cm in dimension was placed inside a horizontal hot-wall reactor, and CH4 was allowed to flow over the foil surface. The coating process was carried out at 600 °C for 20 h. The C coating was formed through thermal cracking of CH4, i.e.,

\[ \text{CH}_4(g) \rightarrow \text{C}(s) + 2\text{H}_2(g). \]

The electrode active-material was derived from Polyacrylic nitrile (PAN)-based activated C fiber received from Taiwan Textile Research Institute. The carbon fiber was subjected to high-energy ball milling at 600 rpm for 3 h. Unless otherwise specified, the active-layer typically contains, on a dry basis, 74 wt.% the activated C powder, 19 wt.% carbon black (CB, Vulcan XC72, Cabot Corporation) and 7 wt.% organic binder (polyvinylidene difluoride; Aldrich). Slurry made from the above ingredients along with N-Methyl Pyrrolidone (NMP) as the solvent was cast onto the current-collector and then dried at 120 °C for 6 h in vacuum. The resulting active-layer was typically ~40 μm thick and weighted ~1.4 mg cm⁻².

The morphologies of the materials and electrodes were characterized by scanning electron microscopy (SEM; LEO1530). The surface area and pore structures of the C fibers were determined by N2 adsorption (Micromeritics; ASAP2010). The X-ray photoelectron spectroscopy (XPS) analysis employed an Al Kα X-ray source operated at 15 kV and 100 W, and used a beam size of 400 μm and pass energy of 20 eV for spectrum acquisition. Sputtering gun was operated at 3 kV and 1 μA with a sputtering area of 2 mm × 2 mm.

2.2. Electrochemical characterizations

Electrochemical characterizations were carried out by using the symmetric cell configuration, which consists of a pair of electrodes having identical size, 0.6 cm in diameter, and active-layer composition. The electrolyte is 1 M LiPF₆ in a 1:2, v/v mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC; Mitsubishi Chemical). All the cells were assembled in a dry room where the dew point was maintained at −40 to −45 °C.

Cyclic voltammetry (CV), galvanostatic charge/discharge, and electrochemical impedance analyses were all conducted on an electrochemical analyzer (Eco Chemie PGSTAT30). For the CV analysis, the cell capacitance \( C_E \) is calculated from:

\[
C_E = \left( \frac{\Delta Q}{\Delta V} \right) = \left( \frac{\int (I/s) dV}{\Delta V} \right),
\]

where \( \Delta Q \) is the total amount of charge accumulated over a voltage window \( \Delta V \), \( I \) is the current, and \( s \) is the linear voltage sweep-rate. The specific capacitance of the active-material, \( C_S \), was calculated from

\[
C_S = 2C_E/m_A,
\]

where \( m_A \) is the mass of active-material on one electrode.

Fig. 1. SEM micrographs of Al current-collectors (a and c) before and (b and d) after the CVD C-coating process.
3. Results and discussion

3.1. C-coated Al current-collector

Fig. 1 compares the surface structures of an Al current-collector before and after C-coating. The pristine Al foil (Fig. 1a and c) possesses a porous surface structure that shows circular pores of ~200 nm in diameter overlapping with one another to form void opening of ~1 μm at surface. After the CVD process, the porous structure remains, while the interior surface is coated with a conformal C layer (Fig. 1b and d). There is a slight increase in void opening, indicating some extent of sintering among the pores during the CVD process. The total deposited C loading is 2.6%, according to elemental analysis (HERAEUS VarioEL-III; NCSH). For brevity, the C-coated Al will be referred to as C-Al.

For XPS analysis (Fig. 2a and b), the Al(2p3/2) spectrum acquired from the fresh surface of the pristine Al foil shows two peaks at 74.3 and 72.5 eV, respectively. The former is typical of Al+3, as in Al2O3, while the later can be assigned to the Al ion with an average valence lower than +3. After sputtering for 120 min, the intensities of above two peaks decrease, while the zero-valent Al peak (71.6 eV) becomes predominant. The intensity of O(1s) (531.7 eV) peak also decreases dramatically after sputtering, echoing with decreasing Al valence. The C(1s) spectrum indicates the presence of mainly C.
(284.6 eV) and a small amount of C=O (288.8 eV) at the fresh surface. The intensities of these signals are low, suggesting that they are most likely surface contaminants from the etching process. No C-containing species is detected after 120 min of sputtering.

On the C–Al current-collector (Fig. 2b), the C(1s) spectrum first displays a peak at 284.6 eV, characteristic of C. With increasing sputtering time, the intensity of the C peak is reducing, while a peak (281.2 eV) attributed to Al4C3 [16] is increasing. Al3C4 becomes the predominant C-containing species after 120 min of sputtering. The Al(2p) peak acquired from the fresh surface can be attributed to Al2O3. After 120 min of sputtering, the peak becomes broadened, and it can be regarded as the combination of Al4C3 (73.7 eV) [16] and Al2O3 (74.4 eV) peaks. The intensity of the Al2O3 (74.4 eV) peak appears unchanged after sputtering. The binding energy of O(1s) (531.7 eV) is typical of O−2. Its intensity also remains essentially unchanged after sputtering, suggesting that the amount of Al2O3 is indeed rather constant.

Based on the XPS data, the following structural models, as schematically drawn in Fig. 3, are proposed for the surface-layers of the pristine Al and C–Al current-collectors. For the pristine Al current-collector (Fig. 3a), the XPS data indicate the presence of a gradient surface oxide layer with decreasing Al valence and oxygen content with depth. For the C–Al current-collector (Fig. 3b), the coated layer consists of mainly a top C layer and a bottom Al4C3 layer. Furthermore, there are two possibilities accounting for the detection of Al2O3 within the coating layer on the C–Al current-collector. For one, the Al3+ and O−2 signals are from certain areas that are not covered by the C deposit. In this case, one would expect the Al and O signals to follow the same trends as observed on the pristine Al (Fig. 2a). This, however, is not observed. For the other, the Al3+ and O−2 signals are from Al2O3 inclusions within the C layer that have been excavated from the original oxide surface-layer due to the formation of the new interfacial carbide phase. These inclusions are likely randomly distributed within the C coating, as schematically shown in Fig. 3b, rendering their signal intensities to remain rather constant with sputtering.

3.2. Activated C fiber

The electrode active-material is derived from the activated PAN-based fiber by high-energy ball milling. The C fiber is porous across its entire cross-section (Fig. 4a). The fiber surface exhibits hierarchical pore structures that consist of large “craters” 50–100 nm in diameter opened at the surface and smaller pores with opening less than 10 nm located inside the craters (Fig. 4b). The pore size distribution determined from N2 adsorption (Fig. 5) shows the presence of a broad distribution below 10 nm with monotonic increase in pore volume with decreasing pore size. Table 1 summarizes the surface area and pore volume data. The BET surface area is 1800 m2/g. The non-micro pore volume, dominated by meso-pores (Fig. 5), is 0.40 cm3/g, which is ~44% of the total pore volume. The presence of a large quantity of meso-pores is beneficial to facilitating diffusion of electrolyte ions within the interior of the carbon framework and hence to the reduction in ionic resistance.
Table 1
Specific surface area and pore volume data for the activated PAN fiber.

<table>
<thead>
<tr>
<th>BET surface area (m² g⁻¹)</th>
<th>BJH surface area (1.7 &lt; d &lt; 300 nm) (m² g⁻¹)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
<th>BJH pore volume (1.7 &lt; d &lt; 300 nm) (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800</td>
<td>567</td>
<td>0.91</td>
<td>0.40</td>
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Fig. 6. Capacitance versus voltage sweep-rate in CV analysis for (curve 1) the cell containing pristine Al current-collectors, and (curve 2) the cell containing C-Al current-collectors. No activated C layer is applied.

3.3. Electrochemical analyses

Fig. 6 shows the plots of capacitance versus voltage sweep-rate for the symmetric cells respectively consisting of pairs of Al and C−Al current-collectors (i.e., no activated C layer was applied in both cases). The C−Al cell exhibits ∼2.5 times higher capacitance at 20 mV/s. This increase may be attributed to the different dielectric properties and interface areas of the surface-layers. The C-coated current-collector appears to have a rougher surface than the uncoated one, as evidenced by the microscopic analysis (e.g., Fig. 1b and d). The most striking difference between these two cells, however, resides in the way their capacitances change with increasing voltage sweep-rate. For the Al cell, the capacitance loses more than 55% as the sweep-rate increases from 20 to 200 mV s⁻¹. In great contrast, the C−Al cell shows less than 7% loss in capacitance even up to 500 mV s⁻¹. Impedance analysis clearly indicates that the Al cell has a higher resistance at all frequencies than the C−Al cell (Fig. 7). This explains why the former exhibits a faster capacitance loss with increasing voltage sweep-rate. The high resistance of the pristine Al electrode is believed to arise from the continuous coverage of an insulating oxide surface-layer, as evidenced by the XPS data (Fig. 2a and 3a).

Fig. 8 plots the voltammograms of the cell made of the electrodes containing the activated C layers on the C−Al current-collectors. The curves are nearly rectangular, showing quick response upon sweep reversal at the two voltage limits. The specific capacitance of the C layer is 140 F g⁻¹ at 20 mV s⁻¹, and it retains 92% (116 F/g) as the sweep-rate increases by 20 folds to 400 mV/s.

Fig. 9 compares the Ragone plots of cells that differ in either active-layer composition or current-collector. For brevity, the cells contain 19 wt.% CB in the active-layer (the standard composition) with Al and C−Al current-collectors are indexed as Al/C(CB) and C−Al/C(CB) cells, respectively, while their counterparts not containing CB as Al/C and C−Al/C cells. The plots were determined by the galvanostatic charge/discharge measurements with current density ranging from 0.5 to 20 A/g. The cell specific energy (SE) and specific power (SP) can respectively be calculated with the following equations.
The Al/C(CB) cell possesses a much smaller resistance at the power maximum. The Nyquist plots for (1) Al/C(CB) cell at 25 °C and (2) Al/C(CB) cell at 25 °C, which imposes additional charge-transfer resistance as compared with the Al/C(CB) cell. The semi-circle corresponds to a RC equivalent circuit, which may be attributed to the resistance and associated capacitance at the Al/C interface. That is, the Al/C(CB) cell possesses a much smaller resistance at the current-collector/active-layer interface than the Al/C(CB) cell. Similar results have previously been reported by Simon et al. [13,14].

According to the XPS data and the structural models for the surface-layers shown in Figs. 2 and 3, the difference in the interface resistance between these two cells may be attributed to the effect of carbon coating on the interface resistance. The one hand, the presence of an insulating oxide layer on the pristine Al current-collector imposes significant resistance to charge transfer. The plot of the Al/C(CB) cell shows a semi-circle within the high-frequency range, which imposes additional charge-transfer resistance as compared with the Al/C(CB) cell. The semi-circle corresponds to a RC equivalent circuit, which may be attributed to the resistance and associated capacitance at the Al/C interface [13]. That is, the Al/C(CB) cell possesses a much smaller resistance at the current-collector/active-layer interface than the Al/C(CB) cell. Similar results have previously been reported by Simon et al. [13,14].

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The improvement in the bulk active-layer conductance by the carbon coating may be explained as follows. In the case of the Al/C cell, because of the presence of the insulating oxide surface-layer, electron current may tend to preferentially flow into (as well as out of) the current-collector through the locations where the oxide layer is relatively thinner. As schematically illustrated in Fig. 11a, instead of taking the shortest paths to flow into the current-collectors, electrons may be forced to take longer pathways in order to reach these preferential locations. This practically decreases the overall electronic conductance of the active-layer. In this case, the conductance can be significantly enhanced as a result of introducing conductive additives within the active-layer. This is exactly observed for the Al/C cell. The possibility that the addition of the CB particles might also result in improved contact between the current-collector and the active-material layer cannot be ruled out. In contrast, when the oxide layer is replaced by the conducting C coating, electrons are allowed to take the shortest paths to flow into the current-collector, as illustrated by Fig. 11b, and hence the overall electronic conductance of the active-layer is reduced.

4. Conclusion

Subjecting etched Al to CH₄ treatment at 600 °C produces a conformal C coating consisting of an Al₄C₃ interfacial layer and a C top layer to replace native oxide layer. When used for supercapacitor applications, the resulting C coating greatly reduce the overall charge-transfer resistance by lowering the interfacial resistance between the current-collector and the active-layer and by enhancing the electronic conductance within the framework of the active-layer. Combining the C-coated Al current-collector with a C fiber active-layer that contains a large mesoporous pore vol-

\[ SE = \frac{1}{2} \frac{C_R n_i^2}{m_A} \]

\[ SP = \frac{1}{2} \frac{C_R n_i}{m_A} \]

where \( C_R \) is the capacitance of the cell and \( m_A \) is the mass of active-material on one electrode.

As shown, for either with or without the addition of CB, the cells employing the C–Al current-collectors (curves 1 and 2) always out perform their counterparts using the pristine Al (curves 4 and 5). The C–Al/C(CB) cell (curve 1) shows the best performance. It exhibits a cell SE of 18 Wh kg⁻¹ under a SP of 25 kW Kg⁻¹ at 25 °C, although the electrolyte composition and separator properties have yet been optimized. Its ESR is 7.8 Ω, and the specific maximum power \( P_{max} \), calculated from

\[ P_{max} = \frac{V^2}{ESR \cdot 2m_A} \]

is ~250 KW Kg⁻¹. At −10 °C (curve 3), the cell retains a SE of 7 Wh kg⁻¹ under 25 KW Kg⁻¹, which is even superior to the performance of the Al/C(CB) cell at 25 °C (curve 4).

Fig. 10 compares the Nyquist plots of the C–Al/C(CB) and Al/C(CB) cells. The addition of excess amount of CB in both cells ensures that the electronic resistance within the framework of the active-layer will not be a limiting factor to charge-transfer. The plot of the Al/C(CB) cell shows a semi-circle within the high-frequency range, which imposes additional charge-transfer resistance as compared with the Al–Al/C(CB) cell. The semi-circle corresponds to a RC equivalent circuit, which may be attributed to the resistance and associated capacitance at the Al/C interface. That is, the Al–Al/C(CB) cell possesses a much smaller resistance at the current-collector/active-layer interface than the Al/C(CB) cell. Similar results have previously been reported by Simon et al. [13,14].

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Acknowledgments

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