Effect of Mesopore in MgO Templated Mesoporous Carbon Electrode on Capacitor Performance

Yasushi SONEDA* and Masaya KODAMA

Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technologies (AIST), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan
*Corresponding author: y.soneda@aist.go.jp

ABSTRACT
Mesoporous carbons (MPCs) with high specific surface area were synthesized by the heat-treatment and subsequent acid treatment of magnesium citrate. The MPCs obtained were examined as electrode materials for electric double layer capacitor and showed the huge gravimetric capacitance with superior rate performance in sulphuric acid electrolyte. The MPCs also realize the larger capacitance than conventional activated carbon in organic electrolyte and extraordinary high retention of capacitance at very low temperature, such as 80% of room temperature value at −60°C.

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1. Introduction

Electric double layer capacitor (EDLC) using carbon electrodes have been anticipated for the future applications, such as power assistance in hybrid electric vehicle, and load levering for pulsed current change in power generator using renewable energy, in which the storage device is required to work with a large and instantaneously fluctuating electric current.1 High surface area carbons are employed for the electrode materials of EDLC to store energy in the electric double layer, and the control of pore size distribution of its carbons is recognized to be one of the most important factors to improve the performance of produced devices.1-4 Although EDLC use high surface area carbon materials on both electrodes (symmetric), the energy storage system using asymmetric (or hybrid) combination of electrode materials have been also extensively studied to enhance the energy density of capacitor device.5 In the case of Li-ion capacitor, graphitic materials for negative electrode which enable to intercalate Li ion into the layered structure are used with porous carbons for positive electrode to accumulate anion on the electrode surface. Therefore, there is strong demand to improve the performance of porous carbons for several types of capacitor devices and the carbon materials with wide variety of morphology and pore structure have been studied extensively.6 One of the successful synthesis methods to control pore size distribution in high surface area carbon is a template carbonization method, in which various kinds of materials are used as template.7

Recently, MgO template method has been developed to synthesize mesoporous carbons (MPCs) with high specific surface area (exceeding 1500 m² g⁻¹) by simple carbonization of mixture of carbon precursor compound and MgO powder.6,9 In this study, we report that the carbonization of pure magnesium citrate gave the formation of high surface area MPCs without conventional activation process and those carbons showed superior capacitive behaviour in both aqueous and nonaqueous electrolytes.

2. Experimental

Figure 1 shows the synthesis steps of MPCs from magnesium citrate. Reagent grade of magnesium citrate (Mg₃(C₆H₅O₇)₂·9H₂O) was heat-treated using a horizontal furnace at elevated temperature (typically 800°C, denote as HTT800) in nitrogen flow for 1 h (heating rate of 5°C min⁻¹). Carbonized solid was immersed into 6 mol dm⁻³ HCl for 25 h at room temperature to dissolve MgO particles in solids. The MPCs thus obtained were washed with distilled water repeatedly and dried in air. For the control of pore size distribution, prescribed amounts of citric acid were added to precursor magnesium citrate and heat-treated as the same procedure.

The thermal behaviour of precursor magnesium citrate was checked by combination of thermogravimetry (TG) and X-ray diffraction measurement (XRD). The porous structure and morphology of MPCs were characterized by nitrogen adsorption isotherm measurement, scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The electrochemical behaviour of MPCs was measured using a three-electrode cell with 40% sulphuric acid electrolyte. The electrode materials (10 mg) were pulverized and mixed with binder PTFE (10 wt%) and carbon black (10 wt%) in mortar, and then the mixture was molded to form a pellet with density of 0.25 g cm⁻³ at 30 MPa for 15 min. The pellet thus obtained was dried at 110°C for 2 h and cooled under vacuum. The weighed pellet was sandwiched with a current collector (Pt mesh) and a glass micro filter in between

Figure 1. (Color online) The synthesis step and the schematic model of mesoporous carbons (MPCs) from magnesium citrate.

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two PTFE plates to compose a working electrode. The measurement cell containing the working electrode was evacuated for 1 h at room temperature and filled with electrolyte under vacuum. Pt plate and Ag/AgCl were used as counter and reference electrode, respectively. The measurement cell was purged with nitrogen flow during the experiment. The gravimetric capacitance with different current density was calculated from 10th discharge curve of galvanostatic charge-discharge cycling. The measurements with sulphuric acid were performed at 25°C.

For the electrochemical measurements in nonaqueous electrolyte, the MPCs from Toyo Tanso Co. Ltd. were also employed as electrode materials (heat-treatment temperature of 900 and 1000°C denoted as HTT900 and HTT1000, respectively). The MPCs, binder PTFE, and carbon black were mixed with the weight ratio of 8:1:1 and formed into a sheet (200 µm thick). Circular electrode materials with 10 mm diameter containing ca. 6 mg of MPC (density of 0.48 g cm\(^{-3}\)) were stamped out from a sheet and placed in a homemade Al laminate test cell with etched aluminium foil current collector for both sides of electrodes (symmetric capacitor). 1 mol dm\(^{-3}\) TEA-BF\(_4\)/PC (tetraethyl ammonium BF\(_4\) in propylene carbonate) was used as electrolyte. The galvanostatic charge-discharge cycling was performed to evaluate the specific capacitance (gravimetric) of EDLC with the current density of 0.2 mA cm\(^{-2}\) between 2.5 and 0 V. The specific capacitance was calculated from the 6th discharge cycles. The measurement was performed between 20 to −80°C, after the test cell was kept at each temperature for 10 h.

3. Results and Discussions

3.1 Synthesis and pore structure of MgO templated carbons

The thermal change of magnesium citrate was pursued by TG and XRD measurements (Figs. 2 and 3). The magnesium citrate decomposed to MgO by the elevation of temperature in three steps, that is, dehydration of crystalline water and dehydration and decarboxylation from ligand components, as shown by TG curve (Fig. 2). XRD patterns from the magnesium citrate with different heat treatment temperature (Fig. 3) indicated that the diffraction of MgO structure was observed the sample treated with 500°C, though the sample with 400°C indicated no crystalline component. The peak width of diffraction from MgO structure was changed very slightly up to 800°C, indicating that the growth of MgO particle size was almost inhibited due to the existence of surrounding carbon matrix. By considering the elemental composition, magnesium citrate is able to form MgO with 19.7 wt% of its weight. However, when it was heat treated in inert atmosphere (nitrogen), parts of ligand citrate produced carbon accompanying the formation of MgO. This situation is also revealed by TG curve since the residual weight at 800°C remained around 24 wt%.

The change of magnesium citrate with heat treatment observed by above measurements was clearly reflected in the synthesis process. The heat treatment of magnesium citrate at 800°C under nitrogen flow resulted in the formation of MgO fine particles distributed in carbon matrix with ca. 25 wt% of yield to precursor. The dissolution of MgO particle from carbon matrix produced finally ca. 9 wt% of carbon materials. The elemental analysis (CHN corder) indicated that the produced carbon contained 89.7 wt% of C, 1.0 wt% of H, and 9.3 wt% of O (difference) and the incombustible, MgO, was not observed in products. This composition is very close to that of activated carbon which was used as a reference.

SEM observation indicated that MPCs thus obtained composed of coagulation of fine particles [Figs. 4(a) and 4(b)]. Figures 4(c) and 4(d) shows TEM photograph of before and after elimination of MgO from heat-treated magnesium citrate. These observations show that opaque MgO particles, which were formed by the heat-treatment, were distributed in carbon matrix uniformly [Fig. 4(c)] and removed effectively by acid treatment [Fig. 4(d)].
Figure 5 compares the N₂ adsorption-desorption isotherm at −196°C on MPC from Mg-citrate and commercial activated carbon (YP17) for EDLC and the BJH analysis of those curves. Both samples show the steep increase of adsorption at very low pressure which indicates the development of micropore. MPC shows additionally large adsorption up to 0.4 of relative pressure, which corresponds to the distribution from small mesopore region. The deference in isotherm of both samples is reflected well in pore size distribution from BJH analysis [Fig. 5(b)]. The specific surface area (BET) of MPC exceeded 2000 m² g⁻¹ and mesopore volume reached 65% of total pore volume (Table 1).

3.2 Capacitance of MPC electrodes in aqueous electrolyte

The capacitive characteristics of MPCs obtained from the mixtures of magnesium citrate and different amount of citric acid were examined in 40% sulphuric acid electrolyte (Fig. 6). The MPC from pure magnesium citrate showed the highest gravimetric capacitance as high as 472 F g⁻¹ at 0.04 A g⁻¹ of current density. Figure 7 shows the cyclic voltammogram (1 mV s⁻¹) of MPC in 40% sulphuric acid electrolyte, indicating the large oxidation current at the upper potential limit and the broad redox peaks around 0.5 V vs. Ag/AgCl. It seemed that the surface functional groups were evolved during the initial sweeps and possessed the role of pseudo-capacitive behaviour in sulphuric acid to show large capacitance.¹⁰,¹¹ The gravimetric capacitance for MPCs from mixed precursor (less than 50 wt% of citric acid) exceeded 400 F g⁻¹ at the galvanostatic discharge current density between 0.04 and 1.0 A g⁻¹ (Fig. 6). Especially, the capacitance at 1.0 A g⁻¹ of current density is quite large and implies the preferable capacitance retention with high rate (current density) usage. The large value of gravimetric capacitance from those carbons could be attributable to the high surface area exceeding 1800 m² g⁻¹ and the value of areal capacitance is the order of 0.22 F m⁻², not very far from the one of the conventional activated carbons. The favourable rate performance is considered due to the large contribution of mesopores to the total pore volume and narrow distribution of them, since the

Table 1. Specific surface area and pore volume of MPCs and activated carbon.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_BET [m² g⁻¹]</th>
<th>V_total [ml g⁻¹]</th>
<th>V_meso [ml g⁻¹]</th>
<th>V_micro [ml g⁻¹]</th>
<th>V_meso/V_total [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPC (Mg-Citrate) HTT800</td>
<td>2113</td>
<td>1.39</td>
<td>0.92</td>
<td>0.47</td>
<td>66</td>
</tr>
<tr>
<td>MPC (Mg-Citrate) HTT900</td>
<td>1530</td>
<td>2.15</td>
<td>1.59</td>
<td>0.56</td>
<td>74</td>
</tr>
<tr>
<td>MPC (Mg-Citrate) HTT1000</td>
<td>1581</td>
<td>2.15</td>
<td>1.56</td>
<td>0.59</td>
<td>73</td>
</tr>
<tr>
<td>MPC (Mg-Citrate/Citric acid = 6/4)</td>
<td>1800</td>
<td>1.22</td>
<td>0.81</td>
<td>0.41</td>
<td>66</td>
</tr>
<tr>
<td>MPC (Mg-Citrate/Citric acid = 9/1)</td>
<td>1429</td>
<td>1.25</td>
<td>0.93</td>
<td>0.32</td>
<td>74</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>1453</td>
<td>0.8</td>
<td>0.14</td>
<td>0.66</td>
<td>18</td>
</tr>
</tbody>
</table>

V_total: adsorption amount of P/P₀ = 0.99, V_meso: cumulative volume by BJH method (adsorption blanch), V_micro: difference between V_total and V_meso.
developed mesopores with suitable size results the fast transport of ions from bulk to solid-electrolyte interface at micropore surface. The rate performance of MPCs from mixture of magnesium citrate with citric acid is slightly better than that of MPC from pure magnesium citrate, though the specific capacitances at low current density are opposite tendency. These observations are seemed to reflect the distribution of micro and mesopores on those materials. The addition of citric acid in precursor resulted in the reduction of micropore volume in products and hence the specific capacitance of MPCs: HTT800, HTT900, and HTT1000, and commercial activated carbon YP17. HTT900 and HTT1000 are courtesy provided by Dr. Morishita at ToyoTanso Co. Ltd.

3.3 Capacitance of MPC electrodes in nonaqueous electrolyte at low temperature

Figure 8 shows the gravimetric capacitance (F g⁻¹) of EDLC with 1 mol dm⁻³ TEA-BF₄/PC electrolyte measured between 20 and −80°C for the MPCs (HTT800, 900, and 1000) with the conventional activated carbon YP17. MPCs showed the larger specific capacitance than YP17 at the entire temperature range under the condition studied. Since YP17 and MPCs have similar amount of micropore volume (Table 1) which may contribute to form the electric double layer, the micropores in MPCs are used more effectively than YP17 because of the existence of mesopores in MPCs. The reduced capacitance of all samples at low temperature may be caused by the increased viscosity of solution and thus decreased ion transfer in the porous channels in solid electrolyte.

Below −30°C, the capacitance of YP17 decreased markedly with lowering the temperature. The MPCs, however, kept the capacitance more than 80% of room temperature until −60°C. This observation is considered to be that the important amount of mesopore volume in MPCs could help the ions transfer from the bulk to the micropore surface even at low temperature.

4. Conclusions

MgO templated carbons (MPCs) which possessed the specific surface area exceeding 2000 m² g⁻¹ with large contribution of mesopore reaching 65% of total pore volume were synthesised by the heat treatment of magnesium citrate and the subsequent elimination of MgO particles. The MPCs showed the quite large capacitance with preferable rate dependence in sulphuric acid electrolyte. The MPCs were also showed the extraordinary high capacitance at low temperature by comparison with a conventional activated carbon. Even at −60°C, MgO carbons showed more than 22 F g⁻¹ of specific capacitance, corresponding with more than 80% of room temperature, although the activated carbon reduced to 8 F g⁻¹, 30% of room temperature. The high performance of MgO templated carbon is considered to be the existence of important amount of mesopore in the materials.

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References