

# Synthesis of MgO templated mesoporous carbons and its use for capacitor electrode

## Síntesis de carbones mesoporosos mediante el método de plantilla con MgO para su uso como electrodos de condensadores

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### Abstract

Mesoporous carbons (MPCs) with large specific surface area are synthesized by the heat-treatment and subsequent acid treatment of magnesium citrate. The MPCs obtained are examined as electrode materials for electric double layer capacitor and show 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.

### Resumen

Se han sintetizado carbones mesoporosos (MPCs) con elevadas superficies específicas mediante tratamiento térmico y posterior tratamiento ácido de citrato de magnesio. Los MPCs obtenidos se han estudiado como electrodos para condensadores de doble capa eléctrica. Estos materiales presentan una capacidad gravimétrica muy elevada y una velocidad de carga-descarga alta en medio ácido sulfúrico. Los MPCs también poseen valores de capacidad en electrolito orgánico mayores que los carbones activados convencionales y presentan una retención de capacidad extraordinariamente alta a muy bajas temperaturas (a una temperatura de -60°C se obtiene una retención de capacidad en torno al 80% con respecto a la capacidad medida a temperatura ambiente).

### 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 flow. 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 [1-3].

Recently, MgO template method has been developed to synthesize mesoporous carbons (MPCs) with high specific surface area (more than 1500 m<sup>2</sup>/g) by simple carbonization of mixture of carbon precursor compound and MgO powder [4, 5]. We found 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. Synthesis and pore structure of MgO templated carbons

Fig.1 shows the synthesis steps and the schematic model of mesoporous carbons from magnesium citrate. Reagent grade of Mg-citrate ( $\text{Mg}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 9\text{H}_2\text{O}$ )

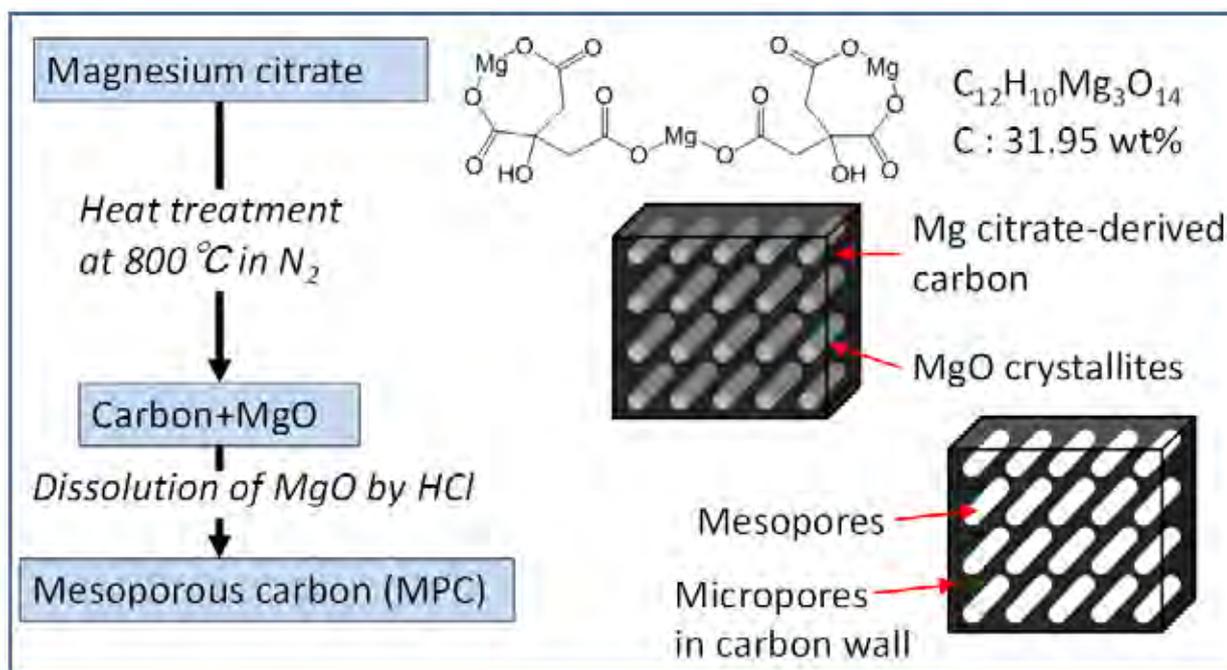
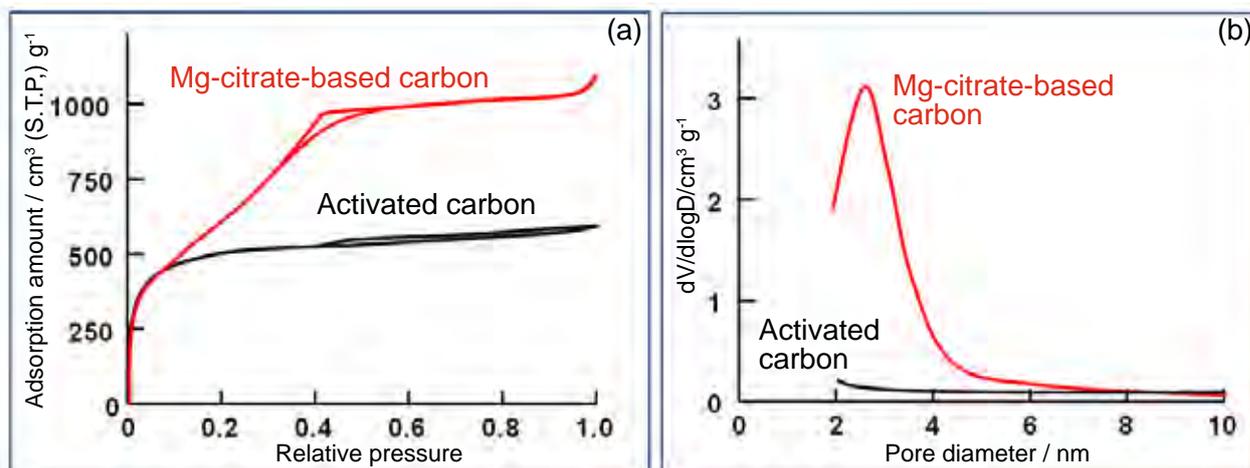


Figure 1. The synthesis step and the structural model of mesoporous carbons (MPCs) from magnesium citrate.

Figura 1. Proceso de síntesis y modelo estructural de carbones mesoporosos preparados a partir de citrato de magnesio.



**Figure 2.** Nitrogen adsorption-desorption isotherm at 77K on MPC from Mg-citrate and commercial activated carbon for EDLC and the BJH analysis of those curves.

**Figura 2.** Isotermas de adsorción-desorción de nitrógeno a 77 K de MPC preparado a partir de citrato de magnesio y de un carbón activado comercial usado para EDLC y análisis BJH de las curvas.

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

**Tabla 1.** Superficie específica y volumen de poros de MPC y del carbón activado.

	$S_{\text{BET}}$ [ $\text{m}^2/\text{g}$ ]	$V_{\text{total}}$ [ml]	$V_{\text{meso}}$ [ml]	$V_{\text{micro}}$ [ml]	$V_{\text{meso}}/V_{\text{total}}$ [%]
MPC (Mg-Citrate)	2085	1.36	0.88	0.48	65
Activated Carbon	1453	0.8	0.14	0.66	18

was heat-treated using a horizontal furnace at 800 °C in nitrogen flow for 1hr (heating rate of 5°C/min). Carbonized solid was immersed into 6 mol/dm<sup>3</sup> HCl for 25 hr to dissolve MgO particles in products and washed with distilled water. According to above simple processes, MPCs with mesopores with narrow distribution which reflects the elimination of MgO particles (template) could be obtained. The organic ligand, citrate, in precursor compound resulted in the formation of carbon skeleton in MPCs with markedly developed micropores.

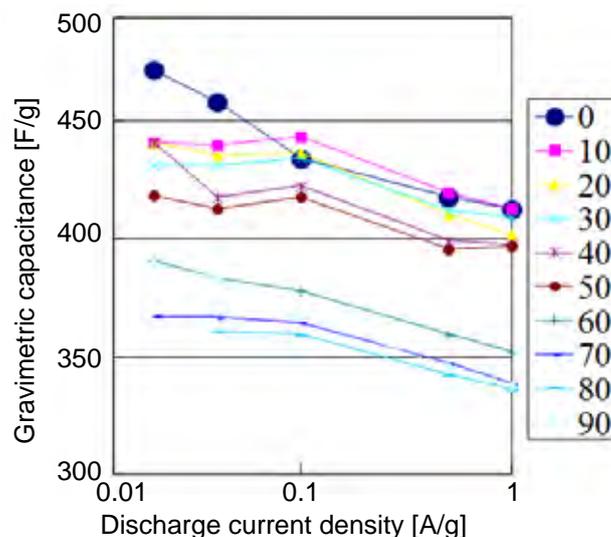
As the same procedure, mixtures of Mg-citrate with several kinds of organic compounds, such as citric acid, magnesium myristate and so on, were used as precursors to control the pore structure (pore size and distribution) in products. By adding the prescribed amount of melamine ( $\text{C}_3\text{H}_6\text{N}_6$ ) monomer in precursor Mg-citrate, the nitrogen enriched MPCs have been synthesized.

Fig.2 compares the  $\text{N}_2$  adsorption-desorption isotherm at 77K on MPC from Mg-citrate and commercial activated carbon for EDLC and the BJH analysis of those curves. Both samples show the step 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 difference in isotherm of both samples is reflected well in pore size distribution from BJH analysis (Fig.2b). The specific surface area (BET) of MPC exceeded 2000m<sup>2</sup>/g and mesopore volume reached 65% of total pore volume (Table 1).

### 3. MPC electrodes in aqueous electrolyte

The capacitive characteristics of MPCs obtained from the mixtures of Mg-citrate and different amount of citric acid were examined in 40% sulphuric acid electrolyte (Fig. 3). The gravimetric capacitance from 10th discharge curve for MPCs (less than 50 wt% of citric acid in precursor) exceeded 400 F/g at the

galvanostatic discharge current density between 0.04 and 1.0 A/g. Especially, the value at 1.0 A/g 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 2000 m<sup>2</sup>/g and the value of areal capacitance is the order of 0.2 F/m<sup>2</sup>, 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 developed mesopores with suitable size results the fast transportation of ions from bulk to solid-electrolyte interface at micropore surface.



**Figure 3.** Dependence of gravimetric capacitance of MPCs synthesized from Mg-citrate with citric acid (0-90 wt.% in precursor) on discharge current.

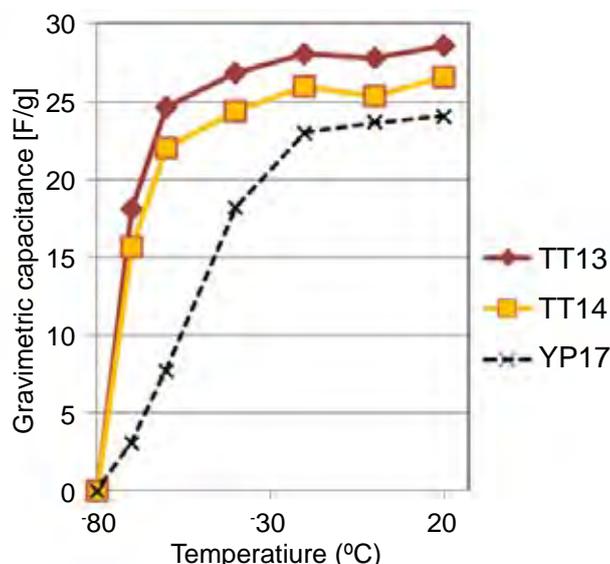
**Figura 3.** Dependencia de la capacidad de MPCs sintetizados a partir de citrato de magnesio y con la adición de ácido cítrico (0-90% en peso en precursor) con la corriente de descarga.

#### 4. MPC electrodes in nonaqueous electrolyte

For the electrochemical measurements in nonaqueous electrolyte, the sample MPCs, binder PTFE and carbon black were mixed with the weight ratio of 8:1:1 and formed into a sheet (100  $\mu\text{m}$  thick). Circular electrode materials with 10 mm diameter 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<sup>3</sup> TEA-BF<sub>4</sub>/PC (tetraethyl ammonium BF<sub>4</sub> 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<sup>2</sup> 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 10hr.

Fig.4 shows the gravimetric capacitance (F/g) of EDLC measured between 20 and -80 °C for the MPCs (TT13 and TT14) with the conventional activated carbon YP17. MPCs showed the larger specific capacitance than YP17 at all the temperatures under this condition. Since YP17 and MPCs have the similar amount of micropore volume which may contribute to form the electric double layer, the micropores in MPCs are used more effectively due to the existence of mesopores. 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 electrode.

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 TT13 and TT14 could help the ions transfer from the bulk to the micropore surface even at low temperature.



**Figure 4.** Gravimetric capacitance at low temperature using laminate cell with Mg-citrate derived mesoporous carbons: TT13 (HTT900), TT14 (HTT1000) and commercial activated carbon YP17.

**Figura 4.** Capacidad gravimétrica a baja temperatura usando una celda plana de aluminio con carbones mesoporosos derivados de citrato de magnesio: TT13 (HTT900), TT14 (HTT1000) y el carbón activado comercial YP17.

#### 5. Conclusions

MgO templated carbons (MPCs) which possessed the specific surface area exceeding 2000 m<sup>2</sup>/g with large contribution of mesopore reaching 65% of total pore volume were synthesised by the heat treatment of magnesium citrate and the subsequent washing out 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 of specific capacitance, corresponding with more than 80% of room temperature, although the activated carbon reduced to 8 F/g, 30% of room temperature. The high performance of MgO templated carbon is considered to be the important amount of mesopore in the materials.

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