

MESOPOROUS CARBONS FOR ENERGY STORAGE

Michio Inagaki, Kaori Ishihara, Masaya Kato and Takahiro Morishita, Aichi Inst Tech, Yakusa, Toyota 470-0392, Japan

Abstract

Mesoporous carbons were prepared through a simple process to heat-treat the mixture of thermoplastic carbon precursor with MgO precursor at 900 °C in Ar gas flow, being followed by the dissolution of MgO using diluted acid. The carbons thus prepared were applied to electric double layer capacitor (EDLC) and gasoline vapor adsorption. The capacitance above 300 F/g with a current density of 20 mA/g was obtained in 1 M H₂SO₄. The carbon with a bi-modal pore size distribution was obtained from the mixture of magnesium citrate and gluconate, which showed an excellent rate performance in EDLC. Mesoporous carbons prepared showed a high gasoline vapor adsorption, more than 1 g of gasoline vapor per 1 g of carbon.

Introduction

Activated carbons have been used since prehistoric era in various applications, based mainly on their adsorptivity [1-4]. Recent development in modern technologies created various novel applications of activated carbons, particularly for energy storage, such as electric double layer capacitors and vehicle canister, which gave sever requirements to activated carbons, not only a high surface area but also a specific pore size distribution [4-6]. In order to meet these requirements, various precursors and activation processes were proposed, which also had to satisfy the requirements from global energy and environment problems. Various preparation processes of porous carbons without any activation process have also been proposed, template process, defluorination of PTFE, carbon aerogels, etc.

One of the present authors (M. I.) was developed a simple process to coat ceramic particles by carbon; the powder mixture of thermoplastic precursor, such as poly(vinyl chloride), poly(vinyl alcohol), etc., and ceramics, such as Al₂O₃, TiO₂, etc., was heat-treated at a high temperature in an inert atmosphere [7,8]. This process was extended to the preparation of porous carbons by using MgO as substrate ceramics and dissolving it out by diluted sulfuric acid [9]. This result suggested us a new preparation process of porous carbons without any stabilization and activation processes even starting from thermoplastic precursors. The preparation of porous carbons with high surface area from various mixtures of carbon precursors and MgO precursors was carried out [9-15], and the resultant porous carbons were applied to the electrode for electric double layer capacitor [12, 13] and the adsorbent for gasoline vapor [14].

In this paper, the process of direct preparation of mesoporous carbons from thermoplastic carbon precursors was proposed, based on the studies on the effects of preparation conditions on pore structure of the resultant carbons. The applications of the mesoporous carbons thus prepared to energy storage, *i.e.*, electric double layer capacitors and adsorption of gasoline vapor were reviewed.

Preparation of mesoporous carbons

The process to prepare mesoporous carbons is shown in **Figure 1b** in comparison with the conventional process to prepare activated carbons in **Figure 1a**. In our process, just one heating process of carbonization is required. The mixture of MgO precursor with thermoplastic carbon precursor is heat-treated at a high temperature in an inert atmosphere to carbonize.

MgO was selected as a substrate ceramics mainly because of its chemical and thermal stability, no structural and compositional changes, no reaction with carbon up to carbonization temperature of carbon precursors, and easily dissolving to diluted acidic solution. Different MgO precursors, MgO itself, magnesium acetate Mg(CH₃COO)₂, magnesium citrate Mg₃(C₆H₅O₇)₂ and magnesium gluconate Mg(C₁₁H₂₂O₁₄) were used. Carbon precursor had to be thermoplastic and so mostly poly(vinyl alcohol) PVA and a coal tar pitch were employed in the present work.

Mixing of two precursors was performed through two processes, powder mixing and solution mixing. Two precursors in different ratios were mixed mechanically in an agate mortar (powder mixing). Aqueous solution of MgO precursors (Mg acetate and citrate) was mixed with the solution of carbon precursor of PVA (10 mass% concentration) in different ratios and then dried at 100 °C in air. The ratio of MgO, which was the mass of MgO expected to be formed from the MgO precursor, to carbon precursor itself was employed as mixing ratio from 1/9 to 9/1 for each combination between MgO precursor and carbon precursor. The mixtures thus prepared were heat-treated at a temperature of 900 °C for 1 h in a flow of Ar. Heating rate up to 900 °C was fixed to be 5 °C/min and flowing rate of Ar gas to be 60 mL/min.

After carbonization at 900 °C, carbon-coated MgO particles were obtained in the form of powder with small size and perfectly black, no white particles of MgO being observed even under optical microscope with a high magnification. The substrate MgO in carbon-coated MgO powders was dissolved out using a diluted acid, either H₂SO₄, HCl, acetic acid or citric acid.

The process proposed here is compared with the conventional process in **Figure 1**. For the preparation of activated

carbon from thermoplastic precursors, the heat treatment in 3 steps, *i.e.*, stabilization, carbonization and activation, is essential. In the present process, however, not only the heat treatment in 1 step but also no weight loss during activation are required.

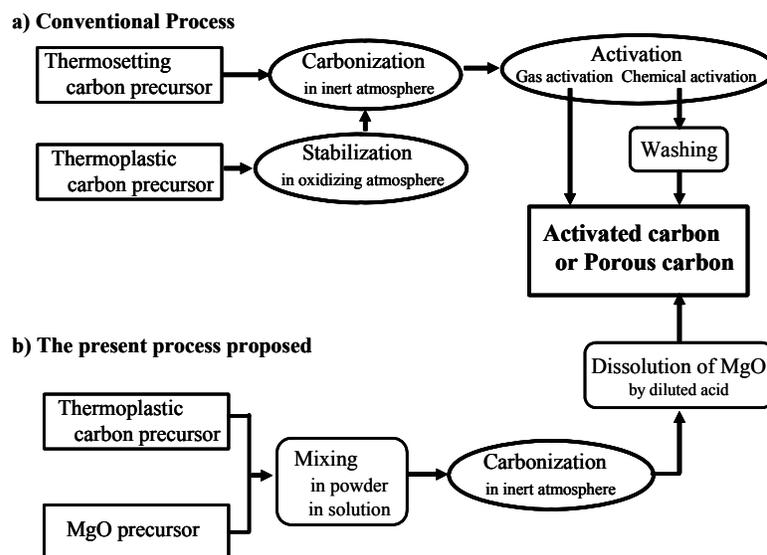


Figure 1. Preparation process of porous carbons.

Table 1. Precursors and their mixing ratio, and pore parameters for carbons prepared.

Mixing method	Precursors	Mixing ratio	S_{BET}	α_s plot analysis		
				S_{total}	$S_{\text{ext.}}$	$V_{\text{micro.}}$
Powder mixing	MgO/PVA	7/3	920	959	137	0.34
		5/5	789	803	156	0.27
		3/7	546	567	110	0.19
Powder mixing	Mg acetate/PVA	7/3	1080	961	510	0.14
		5/5	886	878	412	0.16
		3/7	579	602	319	0.10
Solution mixing	Mg acetate/PVA	7/3	1800	1788	1701	0.10
		5/5	980	966	901	0.04
		3/7	289	321	286	0.01
Powder mixing	Mg citrate/PVA	7/3	1545	1459	1338	0.05
		5/5	1423	1346	1339	<0.01
		3/7	1154	1102	1049	0.02
Solution mixing	Mg citrate/PVA	7/3	1529	difficult to apply α_s nanalysis		
		5/5	1351	1253	1251	0.01
		3/7	1085	1055	958	0.03
Powder mixing	Mg acetate/Pitch	7/3	1187	1140	974	0.07
		5/5	490	477	403	0.03
		3/7	187	181	164	0.01
	Mg citrate/Pitch	7/3	1184	1131	1087	0.01
		5/5	765	759	663	0.03
		3/7	467	471	397	0.02

Pore parameters determined by BET and α_s methods are listed in **Table 1** and pore size distributions are shown in **Figure 2** on some carbons prepared from different precursor mixtures through powder and solution mixing methods.

The carbons obtained are mesoporous and their surface area reach 1500 m^2/g without any activation process. The size

of mesopores depends principally on MgO precursor, Mg acetate, citrate and gluconate giving mesopores with the size of about 12, 5-6 and 2-4 nm, respectively.

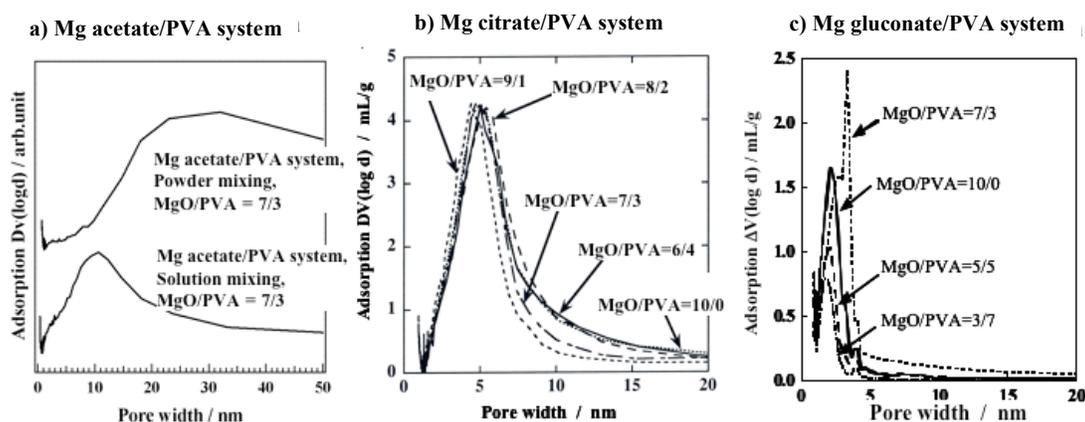


Figure 2. Pore size distributions of the carbons prepared.

Application to electric double layer capacitor

For the determination of the performance in electric double layer capacitor (EDLC), the electrode was prepared by mixing the carbon powder with acetylene black as an electrical conductor and PTFE as a binder in a mass ratio of 80:10:10. The mixture was formed to thin film in approximate thickness of about 100 μm by rolling and then dried at 100 $^{\circ}\text{C}$ for 1 h under vacuum. Three-electrode test cell was used with 1 mol/L H_2SO_4 as electrolyte, Ag/AgCl as a reference electrode and a platinum plate as a counter electrode. For these sample electrodes, the charge-discharge measurement with the potential window from 0.2 to 0.8 V was carried out at room temperature to determine the capacitance of the sample electrode. The current density employed for the measurement of capacitance was 20 ~ 1000 mA/g.

In Table 2, EDLC capacitances with the charging rates of 50 and 1000 mA/g together with microporous and mesoporous surface area, S_{meso} and S_{micro} , determined by BJH method are listed on the samples prepared. Since most of the carbons prepared in the present procedure are mesopore rich, as discussed above, BJH method to analyze the pore structure was employed here.

Table 2. Surface areas and EDLC capacitances of the mesoporous carbons used.

Mixing method	Mixing ratio	Surface area (m^2/g)		EDLC capacitance (F/g)	
		Microporous	Mesoporous	with 50 mA/g	with 1000 mA/g
Powder mixing	MgO/PVA=7/3	764	156	103	34
	MgO/PVA=5/5	706	140	88	39
	MgO/PVA=2/8	355	95	65	28
	Mg acetate/PVA=7/3	378	702	184	96
	Mg citrate/PVA=5/5	304	965	296	144
	Mg citrate/PVA=10/0	270	1410	208	151
	Mg gluconate/PVA=5/5	161	780	191	138
	Mg gluconate/PVA=10/0	124	1014	250	174
	Mg gluconate/Mg citrate=5/5	93	1190	248	198
Solution mixing	Mg citrate/PVA=7/3	372	1248	320	154
	Mg acetate/PVA=7/3	396	1404	300	198
	Mg acetate/PVA=5/5	89	891	238	210
	Mg acetate/PVA=2/8	44	245	89	68

Carbon powders obtained showed relatively high EDLC capacitance, in comparison with the values reported on various activated carbons with high BET surface area. The carbon prepared from the mixture of Mg acetate with PVA in 7/3 through

solution mixing gave very high capacitance as 320 F/g with the current density of 50 mA/g, which may be due to high S_{meso} , as 1250 m²/g, but the same mixture through powder mixing gave only 190 F/g and 700 m²/g, respectively. The carbons prepared from the mixtures of Mg citrate with PVA, which had very high mesoporous surface area either through powder or solution mixing, had relatively high capacitance, as high as 300 F/g with 50 mA/g and 140 F/g with 1000 mA/g.

For some of the carbons prepared, the dependence of EDLC capacitance on current density was shown in **Figure 3**, together with an activated carbon being commercially available. For most of carbons prepared, capacitance decreases with increasing current density very rapidly up to 200 mA/g, but very gradually above 200 mA/g. The carbon prepared from the mixture of Mg acetate with PVA in 7/3 through solution mixing gives a high capacitance as 340 F/g with current density of 20 mA/g, but its capacitance decreases to about 220 F/g with 200 mA/g. Above 200 mA/g, its capacitance decreases slightly and becomes 200 F/g with 1000 mA/g. For the carbons prepared by solution mixing, which contained a large amount of mesopores, capacitances at large current density didn't decrease so much, comparing with those at low current density. The carbon prepared from Mg acetate/PVA mixture in 5/5 with solution mixing showed 240 F/g with a current density of 20 mA/g, which was not the highest in the present samples, but gave 210 F/g with 1000 mA/g, only 16 % decrease from that with 20 mA/g. This is probably due to a large mesoporous surface area S_{ext} , more than 90 % of total surface area S_{total} ($=S_{\text{meso}}+S_{\text{micro}}$), in other words, a large development of mesopores.

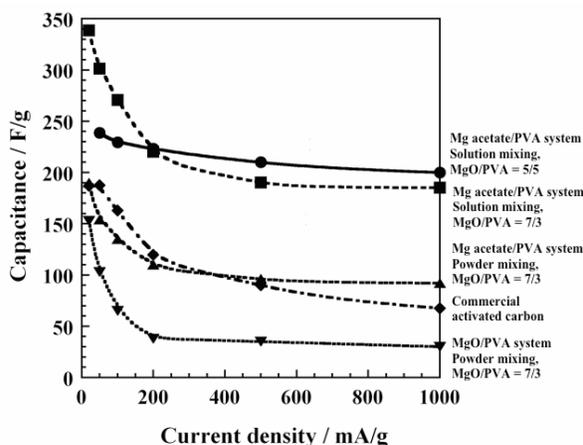


Figure 3. Dependences of capacitance on current density.

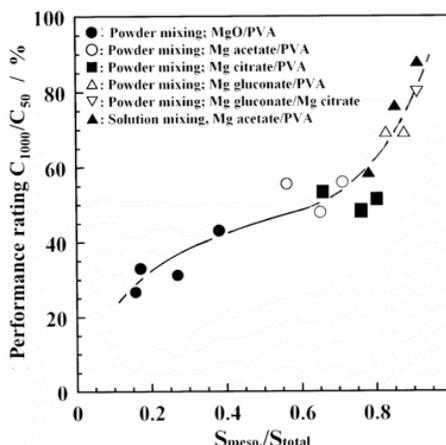


Figure 4. Relation between performance rating C_{1000}/C_{50} and relative mesoporous surface area $S_{\text{meso}}/S_{\text{total}}$.

In **Figure 4**, performance rating defined by the ratio of the capacitance with 50 mA/g to that with 1000 mA/g, C_{1000}/C_{50} , is plotted against the ratio of mesoporous surface area S_{meso} to total surface area S_{total} , $S_{\text{meso}}/S_{\text{total}}$.

Performance rating C_{1000}/C_{50} depends strongly on relative mesoporous surface area $S_{\text{meso}}/S_{\text{total}}$, showing gradual increase in intermediate range of $S_{\text{meso}}/S_{\text{total}}$ from 0.4 to 0.8. Above 0.8 of $S_{\text{meso}}/S_{\text{total}}$, C_{1000}/C_{50} increases very sharply. It is worthwhile to mention that the dependence of C_{1000}/C_{50} is common for the carbons prepared by using different MgO precursors.

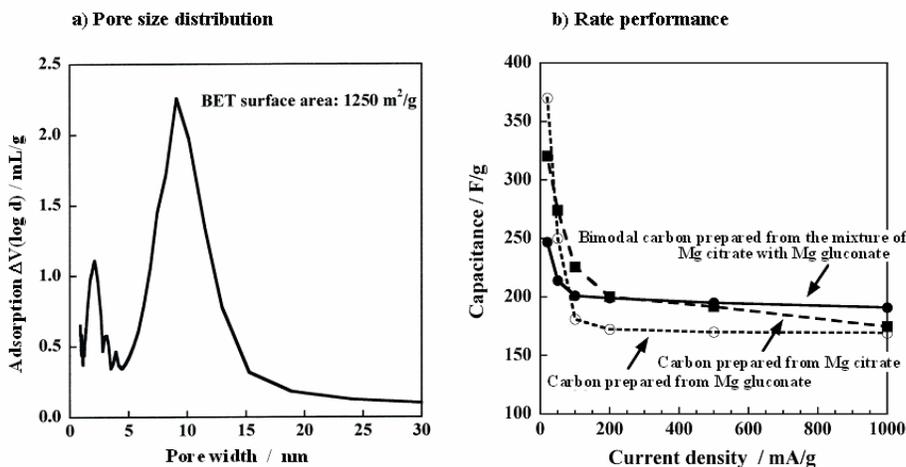


Figure 5. Pore size distribution and rate performance of capacitor on a bi-modal carbon.

A carbon with bi-modal pore size distribution, as shown in **Figure 5a**, was obtained from the mixture of Mg citrate with Mg gluconate, of which pore structure parameters and EDLC capacitance are listed in **Table 2**. It showed an excellent rate performance in 1 mol/L H₂SO₄ electrolyte, as shown in **Figure 5b**, performance rating reaching about 80 %. Although more detailed studies using electrode carbons with different pore structures are required, this result suggests the importance of exact pore structure control in electrode carbon.

Application to gasoline vapor storage

For the carbons obtained from the systems of Mg acetate/PET and Mg citrate/PVA through powder mixing, adsorption of gasoline vapor was measured by hanging the sample carbon in a gasoline reservoir, as schematically shown in **Figure 6a**. The weight increase was followed with time, which was reasonably supposed to be due to the adsorption of gasoline vapor at room temperature, as shown in **Figure 6b**.

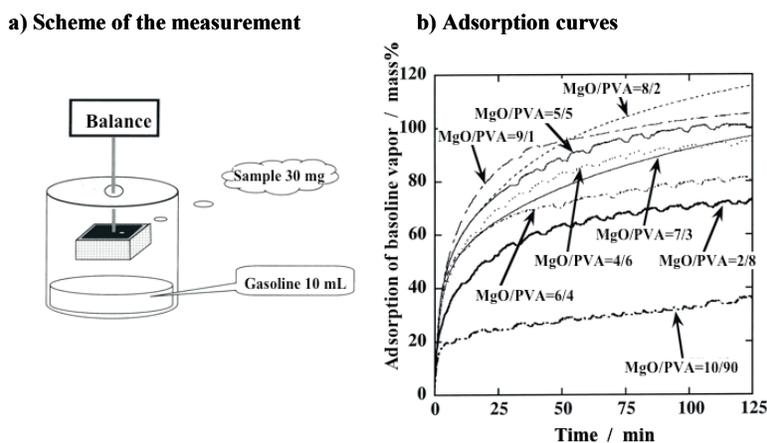


Figure 6. Measurement of adsorption of gasoline vapor.

The weight increase due to adsorption of gasoline vapor seemed to be saturated, as shown in **Figure 6b**. In the present work the adsorbed amount after 125 min, ΔW_{125} , was employed as a measure of adsorptivity of gasoline vapor.

In **Figure 7**, the carbons prepared from the mixtures of Mg acetate with PET and those of Mg citrate with PVA in different mixing ratios are compared with a commercially available activated carbon by plotting ΔW_{125} against the volume of the pores with the size of less than 10 nm, $V_{<10}$. Adsorptivity of the carbons prepared from Mg citrate/PVA mixtures, of which pores have a high population at the size of about 5 nm (see **Figure 2b**), is very high, almost the same mass of gasoline as adsorbent carbon being able to be adsorbed. On the other hand, the carbons prepared from Mg acetate/PET mixtures with a broad size distribution of mesopores (see **Figure 2a**) showed relatively low adsorptivity. The relation between ΔW_{125} and $V_{<10}$ may be approximated to be linear.

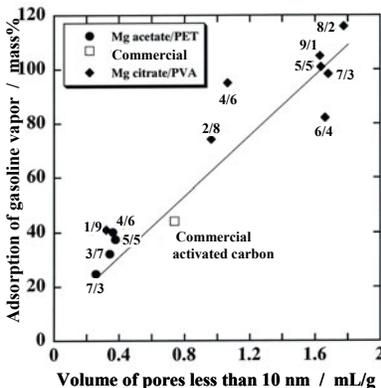


Figure 7. Relation between adsorptivity for gasoline vapor ΔW_{125} and pore volume $V_{<10}$.

Conclusion

Mesoporous carbons were successfully prepared through a simple process; heat treatment of the mixtures of MgO precursor and thermoplastic carbon precursor, followed by the dissolution of MgO by diluted acid. The mesoporous carbons obtained were successfully applied for electric double layer capacitor and storage of gasoline vapor. The same procedure was extended to the preparation of carbon-coated metallic tin of fine particles for the anode of lithium ion rechargeable batteries [16] and to that of carbon-coated tungsten and molybdenum carbides for electrochemical capacitors [17].

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