Capacitance Behavior of Ordered Mesoporous Carbon/Fe₂O₃ Composites: Comparison Between 1D Cylindrical, 2D Hexagonal, and 3D Bicontinuous Mesostructures

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Abstract

The combination of high electronic conductivity, enhanced ionic mobility, and high pore volume make ordered mesoporous carbons promising scaffolds for active energy storage materials. However, mesoporous morphology and structural stability needs to be more thoroughly addressed. In this paper, we demonstrate Fe₂O₃ impregnation into 1D cylindrical (FDU-15), 2D hexagonal (CMK-3), and 3D bicontinuous (CMK-8) symmetries of mesoporous carbons. We use these materials for a systematic study of the effect of mesoporous architecture on the structure stability, ion mobility, and performance of mesoporous composite electrodes. By optimization of the porous structure, the oxide impregnation enabled relatively high performance: > 650 F g⁻¹ of Fe₂O₃ and > 200 F g⁻¹ total capacitance. This work highlights the new considerations of structure degradation in different pore symmetries with active material impregnation and its effect on ion mobility and electrochemical performance in porous scaffold electrodes. The results show that the most commonly used 2D CMK-3 is not suitable as a host material due to its poor structure stability and ion mobility, while the 1D FDU-15 and 3D CMK-8 have their own merits related to framework stability and porous structures.

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1. Introduction

Since the first synthesis in 1999 [1], ordered mesoporous carbons (OMCs) have been widely used as host materials for metal [2, 3], metal oxide [4-7], sulfur [8-10], or polymers [11] for electrochemical sensors [11, 12], fuel cells [2, 3], supercapacitors [4-7, 13, 14], lithium ion batteries [15-17], Li-O batteries [18], and Li-S batteries [8-10] due to their high corrosion resistance, good electrical conductivity, high surface area, large pore volume, and easy handling. In addition, the well-defined porous dimensions were found to enable controlled metal or metal oxide nanoparticles impregnation into the porous scaffold [2], facilitating higher material utilization for catalysis and energy storage. For example, Shi *et al.*, impregnated MnO₂ nanoparticles into mesoporous CMK-3 carbon and demonstrated a capacitance of 600 F g⁻¹ MnO₂ [6]. Similarly, many other metal oxide nanoparticles, such as Nb₂O₅ [4], Fe₂O₃ [5], and Cu₂O [7] showed enhanced electrochemical performances when impregnated into mesoporous CMK-3, compared to their pristine oxide counterparts. The enhanced performance was attributed not only to the better conductivity and small particle size, but also to the well-defined pore structure which facilitated the rapid ion mobility via meso-channels.

To date, most of the OMC related composites were based on CMK-3 which is made by mesoporous silica SBA-15 as hard template [2, 3, 5-7, 11, 12, 14, 17, 18]. The mesostructure of CMK-3 is maintained by the inter-pillars nano-bridges which were derived from the micropores (< 2nm) in the original silica templates [19]. These nano-bridges are very fragile upon heterogeneous nanoparticle loading process, which could potentially break the mesostructure of CMK-3 and will further affect the accessibility of active species and electrochemical performance. However, this mesostructure stability issue has never been investigated.

Along with the stability, it is expected that other porous parameters of OMCs can also influence the electrochemical performance of OMC based composites, especially pore shape which can strongly affect ion mobility inside the pores. Therefore, a systematically comparison of electrochemical behaviors between different structured OMC composites is essential for a better understanding of the effects of pore structures on the performance. However, very few reports deal with non-CMK-3 composites and they all lack detailed

investigation of the mesostructure's influence on the application [4, 8-10, 13, 15, 16]. Hence it is important to design controlled experiments with various OMCs structures synthesized and tested under similar conditions in order to better understand and optimize OMCs related composites based on their structure stabilities and porosities.

Iron oxide is one of the cheapest common oxides with very low toxicity, which made it a good candidate for anodes in Li- or Na- ion batteries [20-25]. Furthermore, the operating voltage window for iron oxide faradaic activity is lower than other commonly used metal oxides, which makes it one of the promising anode materials for high energy density asymmetrical supercapacitors [26]. Additionally, studies have shown that the capacitive performance of iron oxide strongly depends on the ion mobility [27, 28]. In light of that, we chose OMC/iron oxide composites as the model system to study the influence of structure on ion mobility and electrochemical performance.

In this work, we have synthesized 1D *p6mm* FDU-15 [29], 2D *p6mm* CMK-3 [19], and 3D *Ia3d* CMK-8 [30] by soft or hard template methods, and impregnated different amounts of Fe₂O₃ nanoparticles inside the mesopores using a uniform nanoparticle loading procedure. The pore structures and stabilities were characterized by N₂ adsorption-desorption and transmission electron microscope (TEM), and the effect of structure on ion mobility was studied by electrochemical impedance spectroscopy (EIS). The capacitance performance of different mesostructures with different Fe₂O₃ % was evaluated by cyclic voltammetry (CV) and the relationship between mesostructure, pore stability, ion mobility, and electrochemical performance were systematically investigated.

2. Experiment section.

2.1. Materials Preparation.

1D cylindrically structured FDU-15 was synthesized by a soft template method according to Ref. [29], using triblock copolymer Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆, MW=12600) as structure directing reagent and urea and formaldehyde as the carbon source. In a typical process, 1 g F127 was dissolved in 8.0 g ethanol. Then 5 g of 20 % resol precursors, prepared by literature method [29], were added to the solution. The mixture was stirred

for 1 h and then transferred to a glass Petri dish, and left for 5–8 h at room temperature and 24 h at 100 °C to evaporate the ethanol. Then the gel was thermopolymerized in a 180 °C oven for 12 h. The as-made product was collected and ground into fine powder. Calcination was carried out in a tubular furnace at 600 °C for 3 h and subsequently 900 °C for 2 h under Ar flow. The heating rates were 1 °C min⁻¹ below 600 °C and 5 °C min⁻¹ above 600 °C.

2D hexagonally structured CMK-3 was synthesized by using mesoporous silica SBA-15 as a hard template [19]. The detailed synthesis method of SBA-15 was described in Ref. [31]. The carbon nanocasting process was as follows: 1.2 g of SBA-15 was added to a solution made of 1.5 g sucrose, 0.17 g of H₂SO₄, and 6 g H₂O. The mixture was dried in oven at 100 °C for 6 h, and subsequently 160 °C for another 6 h. The silica sample containing partially carbonized sucrose was treated again with a mixture of 0.96 g of sucrose, 0.11 g of H₂SO₄ and 6 g of H₂O, followed by a same drying process at 100 °C and 160 °C. The carbonization was carried out in a tubular furnace at 600 °C for 3 h, and subsequently 900 °C for 4 h under Ar flow, the heating rates were 1 °C min⁻¹ below 600 °C and 5 °C min⁻¹ above 600 °C. The silica was etched away by a 3 M NaOH solution three times at 50 °C. The template-free carbon product thus obtained was centrifuged and washed by D. I. water.

3D bicontinuous CMK-8 was also synthesized by a hard template method, with mesoporous silica KIT-6 as a template. The KIT-6 was synthesized according to Ref. [32], with the molar ratio of 0.017 P123 / 1.67 TEOS / 1.67 *n*-butanol / 1.83 HCl / 195 H₂O. The carbon nanocasting process was similar to CMK-3, with adjusted sucrose and sulfuric acid amounts to fit the pore volume of KIT-6. In brief, 1.2 g of KIT-6 was infiltrated by 1.17 g sucrose, 0.13 g of H₂SO₄, and 4.7 g H₂O. After drying in an oven at 100 °C for 6 h, and 160 °C for another 6 h, the sample was treated again by a mixture of 0.62 g of sucrose, 0.07 g of H₂SO₄ and 3.85 g of H₂O, followed by the same drying process at 100 °C and 160 °C. The annealing process and silica removal processes were the same as CMK-3.

To improve the hydrophilicity of mesoporous carbon before electrochemical testing or Fe₂O₃ loading, all three kinds of mesoporous carbon were treated with 70 % HNO₃ at 60 °C for 1 h and subsequently washed by D. I. water.

In order to grow Fe₂O₃ nanoparticles inside mesopores, the carbons were soaked in an Fe(NO₃)₃ aqueous solution and a low pressure vacuum filtration process was used to remove any extra salt solution outside the mesopores. The mesoporous carbon with Fe(NO₃)₃ solution was heated to 100 °C for 6 h to evaporate water, followed by 190 °C annealing in argon flow for 5 h to decompose Fe(NO₃)₃ into Fe₂O₃. The loading amount of Fe₂O₃ was controlled by the concentration of Fe(NO₃)₃ solutions, which ranged from 3 % to 45 %. The final products were noted as FDU-15-x, CMK-3-x, and CMK-8-x, where x was the weight % of Fe₂O₃ measured by ICP-OES.

2.2. Characterization.

X-ray diffraction (XRD) patterns were recorded by Bruker Smart1000 (Bruker AXS Inc., USA) using CuK α radiation. XPS analysis was done on a Kratos AXIS 165 spectrometer. The C 1s peak was calibrated at 284.8 eV. Images of OMCs and OMC/Fe₂O₃ composites were acquired using a transmission electron microscope (JEOL JEM 2100 FE-TEM).

Nitrogen (N₂) adsorption-desorption isotherms were recorded with a Micromeritics ASAP 2020 Porosimeter Test Station. Samples were degassed (in vacuum) at 100 °C for 12 hours before the test. The specific surface areas were calculated using the BET method from the nitrogen adsorption data in the relative pressure range (P/P₀) of 0.05–0.20. The porosity distribution was calculated from adsorption branch using the BJH (Barrett–Joyner–Halenda) equation.

The loading amount of Fe₂O₃ was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) characterization performed on a Perkin Elmer ICP Optima 4700. Intensities were measured at 259.939 nm for Fe. OMC/Fe₂O₃ samples were dissolved in a freshly prepared concentrated HCl/ethanol solution and diluted to a known volume before being administered to the plasma. The final concentration of HCl and ethanol were 2 % and 0.8 %, respectively.

2.3 Electrochemical Measurement.

All the electrochemical studies were performed in a standard three-electrode system utilizing a bipotentiostat (BI-STAT, Princeton Applied Research). The electrolyte was 1 M Na₂SO₃ aqueous solution. Ag/AgCl was used as the reference electrode and glassy

carbon was used as the counter electrode. To make the working electrode, a slurry of the mesoporous material, carbon black, and a poly-(vinylidene fluoride) (PVDF) binder at a weight ratio of 85:10:5 dispersed in N-Methyl-2-pyrrolidone (NMP) was cast onto a stainless steel foil with a loading of 0.5–1.0 mg/cm² using a doctor blade. After an overnight drying in a vacuum oven at 100 °C, the active materials were pressed on a nickel foam current collector. The potential window was -0.8 V to 0 V vs. Ag/AgCl. Electrochemical impedance spectroscopy (EIS) was also conducted with a frequency range from 20 kHz to 10 mHz at -0.15 V vs. Ag/AgCl.

3. Results and discussions.

3.1 Structural and Textural Characterization of different structures

OMC/Fe₂O₃ composites

X-ray photoelectron spectroscopy (XPS) was used to determine the valence state of the iron oxide. In order to get a good intensity, the samples with highest Fe₂O₃ % were characterized and the results in the Fe 2p spectra region are shown in Figure S1. Regardless of the mesostructures, all of the samples show similar spectra; the broader peaks at 711 eV, 719 eV and 724 eV were in agreement with the reported value for Fe₂O₃ [33]. Due to the low anneal temperature of 190 °C and the small particle size, the Fe₂O₃ nanoparticles have poor crystallinity and no peak can be detected by XRD (data not shown).

The mesostructure of the three different OMCs and their derived OMC/Fe₂O₃ composites were compared by N₂ adsorption–desorption isotherms. The black curves in Figure 1 a-c shows isotherms of OMCs, which are all type-IV curves with typical mesoporous characteristics at P/P₀ of 0.4-0.6 [34]. The pore parameters of OMCs are listed in Table 1. Although the pore diameter of CMK-3 (3.2 nm) is smaller than that of FDU-15 and CMK-8 (3.8 nm), the difference is fairly small, and is not expected to dramatically affect Fe₂O₃ loading and capacitance performance. It is noteworthy that the CMK-3 and CMK-8 made by hard template method have much larger surface area than the soft templated FDU-15. Additionally, the pore volume of CMK-3 (0.907 cm³ g⁻¹) and CMK-8 (1.178

$\text{cm}^3 \text{g}^{-1}$) are about 2 fold higher than FDU-15 ($0.327 \text{ cm}^3 \text{g}^{-1}$). The small pore volume of FDU-15 limits the possible loading amount of Fe_2O_3 , hence, the highest mass loading of Fe_2O_3 in FDU-15 was only 20 %, compare with nearly 50 % Fe_2O_3 content in the other two OMCs.

The trend of structure change upon impregnation of Fe_2O_3 into various OMCs were characterized by N_2 adsorption–desorption, which are shown in Figure 1 a-c. Based on the isotherms, the pore size distributions and detailed structure parameters are calculated and presented in Figure 1 d-f and in Table 1, respectively. Upon Fe_2O_3 loading, the microporous volume did not change much in all of three mesostructures, indicating that the Fe_2O_3 was mainly formed in the mesopores. For the 1D mesoporous FDU-15 based materials, pore diameters remained stable but there was a small decrease of mesopore volume which occurred with the increase of Fe_2O_3 %. However, for the 3D mesoporous CMK-8 based composites, a dramatic decrease of mesopore volume happened during Fe_2O_3 loading, and the mesoporosity disappeared at Fe_2O_3 % of 47.1 %. The pore size and mesopore volume was even more significantly decreased in the 2D mesoporous CMK-3 based materials, and the composite lost its mesoporosity at only 19.7 % of Fe_2O_3 content.

In order to quantitatively characterize the variation of mesopore volume in different mesostructures during Fe_2O_3 incorporation, we have calculated the absolute (ΔV_{meso}) and relative (ΔV_{meso} %) mesopore volume difference between OMC/ Fe_2O_3 composites and their corresponding OMCs (see supporting information for the calculation method) and compared them in Table 1. Considering the densities of Fe_2O_3 nanoparticles are same regardless of the host material mesostructures, the mesopores' volume decrease should be similar in different OMCs. However, the trend of mesoporosity lost was quite different between soft templated OMC (FDU-15) and hard templated OMCs (CMK3 and CMK-8). For same level of Fe_2O_3 %, the ΔV_{meso} of FDU-15/ Fe_2O_3 was one order of magnitude lower than ΔV_{meso} of CMK-3/ Fe_2O_3 and CMK-8/ Fe_2O_3 . Therefore, some factor other than Fe_2O_3 accommodation was responsible for the mesoporosity decrease in the hard templated OMCs/ Fe_2O_3 .

Figure 1 N₂ adsorption–desorption isotherms (a–c) and pore size distributions (d–f) of OMCs and their derived OMC/Fe₂O₃ composites: (a, d) FDU-15 system, (b, e) CMK-3 system, and (c, f) CMK-8 system.

TEM was carried out to further investigate the influence of Fe₂O₃ impregnation on the evolution of the OMCs' mesostructure. Figure 2 compared TEM images of the three different OMCs with various loading amounts of Fe₂O₃. As demonstrated, FDU-15

maintained its parallel mesostructure, while the ordered mesoporous architecture of CMK-3 and CMK-8 degraded upon impregnation of oxide material. The clear loss of the ordered mesostructure after loading of 19.7 % of Fe₂O₃ in CMK-3 (Figure 2f) and 47.1 % of Fe₂O₃ in CMK-8 (Figure 2k) is in very good agreement with the results obtained from the N₂ adsorption–desorption isotherms discussed above, hence we attributes the change of pore volume and pore size distribution to the destruction of the mesoporous architecture upon loading of oxide.

Table 1 N₂ adsorption–desorption properties of OMCs & OMC/Fe₂O₃ composites*

Sample ID	d (nm)	S_t (m ² g ⁻¹)	V_t (cm ³ g ⁻¹)	V_{meso} (cm ³ g ⁻¹)	V_{micro} (cm ³ g ⁻¹)	ΔV_{meso} (cm ³ g ⁻¹)	ΔV_{meso} (%)
FDU-15	3.8	554	0.327	0.311	0.016	-	-
FDU-15-7.8	3.9	593	0.263	0.248	0.015	0.043	13.8
FDU-15-20.0	3.8	564	0.216	0.199	0.017	0.064	20.7
CMK-3	3.2	1266	0.907	0.873	0.034	-	-
CMK-3-8.1	2.4	819	0.442	0.392	0.050	0.448	51.3
CMK-3-19.7	< 1.7	672	0.184	0.147	0.037	0.692	79.2
CMK-3-49.9	< 1.7	380	0.032	0.020	0.012	0.834	95.6
CMK-8	3.8	992	1.178	1.158	0.020	-	-
CMK-8-7.6	3.9	958	0.858	0.836	0.022	0.256	22.1
CMK-8-21.4	3.8	707	0.415	0.394	0.021	0.661	57.1
CMK-8-47.1	< 1.7	469	0.153	0.123	0.030	0.932	80.5

* All data are calculated from adsorption branch:

d : pore diameter;

S_t and V_t : total surface area and pore volume;

V_{meso} : mesopore (2 nm < d < 50 nm) volume;

V_{micro} : micropore (d < 2 nm) volume;

ΔV_{meso} : mesopore volume change after Fe₂O₃ loading based on carbon mass.

ΔV_{meso} %: normalized mesopore volume change after Fe₂O₃ loading based on original carbon.

Figure 2 TEM images of different meso-structure OMCs & OMC/Fe₂O₃ composites: (a) FDU-15, (b) FDU-15-7.8, (c) FDU-15-20.0, (d) CMK-3, (e) CMK-3-8.1, (f) CMK-3-19.7, (g) CMK-3-49.9, (h) CMK-8, (i) CMK-8-7.6, (j) CMK-8-21.4, and (k) CMK-8-47.1. All scale bars are 100 nm.

Considering the results from N₂ adsorption-desorption and TEM together, it is clear that the different mesostructure variations were caused by the different stabilities of the carbon framework. For 1D FDU-15 made by the soft template method, the carbon is reported to grow around the surfactant micelles, which formed the rigid carbon network [29]. On the other hand, for the 2D CMK-3 and 3D CMK-8 made from the hard template method, the adjacent pillars in CMK-3 or two sets of carbon networks in CMK-8 were connected by nano-bridges which were derived from the micropores (< 2 nm) in the original SBA-15 or KIT-6 silica templates [19, 35]. We attribute the destruction of the mesoporous structure in the 2D and 3D OMCs to the fragility of those nano-bridges: during the solvent evaporation or salt decomposition in Fe₂O₃ growth process, the released gases (H₂O and NO_x) as well as volume changes during the Fe(NO₃)₃ to Fe₂O₃ transformation could easily break the nano-bridges and cause the collapse of mesoporous architecture. While in FDU-15, the rigid carbon framework could prevent the collapse and maintain the structure and pore size. Furthermore, when comparing the ΔV_{meso} % of

the two types of hard template derived OMCs, it is noteworthy that more mesopores volume was kept in CMK-8/Fe₂O₃, indicating a more stable mesostructure in CMK-8. This might be because the 3D carbon network in CMK-8 can help to maintain the mesostructure after the inter-framework bridge collapse. Overall, the mesostructure stability upon Fe₂O₃ loading is 1D FDU-15 > 3D CMK-8 > 2D CMK-3. The trend of structural stability is also evident in the surface area variation between OMCs and their derived OMC/Fe₂O₃. For FDU-15, when introducing small amount of Fe₂O₃ nanoparticles in the mesopores, the inner surface roughness of mesopores is increased, leading to a larger surface area of FDU-15-7.8 than FDU-15. Further increases in Fe₂O₃ loading then slightly decrease surface area due to the increased nanoparticle size and composite density. However, in the case of the CMK-3 and CMK-8 systems, owing to the unstable mesostructures, the rapid loss of mesoporosity leads to dramatically decreased surface areas which overwhelm any surface roughness increase with increased Fe₂O₃ %.

3.2 Electrochemical studies of different structures of OMC/Fe₂O₃ composites

3.2.1 Electrochemical impedance spectroscopy (EIS) studies of mesostructure's influence on ion mobility.

EIS was used to evaluate the effects of mesostructure on the ion mobility inside the mesoporous systems. Figure 3 a-c shows Nyquist plots of OMCs and OMC/Fe₂O₃ composites. Qualitatively, all plots are similar in shape, beginning with a semi-circle or arc at high frequencies, followed by a straight line inclined at an angle of around 45° to the real axis in the medium frequency region, and a nearly vertical line in the low frequency region. Previous work suggested that such a pattern of the EIS can be fit by an equivalent Randles circuit [26, 28, 36-45], as shown in the inset of Figure 3a.

Comparing different samples, the solution resistance (R_s) showed similar values (~ 2.2 Ω) for all the measured EIS. For the materials with same mesostructure, the charge transfer resistance (R_{ct}) slightly increased with raising Fe₂O₃ % in the OMC/Fe₂O₃ composites.

This is because the Faradaic processes at Fe_2O_3 are normally slower than the ion adsorption at the carbon surface. Comparison of different mesostructured OMC/ Fe_2O_3 composites with similar Fe_2O_3 %, *e.g.*, FDU-15-7.8, CMK-3-8.1, and CMK-8-7.6, demonstrated very similar R_{ct} values, indicating comparable redox reactivity of Fe_2O_3 among these samples.

The straight line with 45° angle at the medium frequency region ascribes to the Warburg impedance (Z_w), which reflects the ion transportation process in the porous electrode. As listed in Table 2, unlike R_s and R_{ct} , Z_w were quite different in each sample, implying a large difference of ion mobility in diverse pore architectures. The trend of Z_w in the various OMCs is 1D FDU-15 (0.8Ω) < 3D CMK-8 (2.0Ω) < 2D CMK-3 (2.5Ω), indicating better ionic mobility in the 1D mesostructure. This is because of the small tortuosity of 1D channels (~ 1) compared with 2D and 3D structures (> 1). Introducing Fe_2O_3 would add surface roughness which will slightly increase the tortuosity of the mesopores, and should lead to a small decrease in the ion mobility inside the pores. As expected, the Z_w increased in FDU-15-7.8 (1.4Ω) and FDU-15-20.0 (2.1Ω). However, the value of Z_w in FDU-15/ Fe_2O_3 was still very small even compared with bare CMK-3 and CMK-8, indicating that a clear ionic pathway was maintained in the FDU-15 structure, even at high mass loading amounts. On the contrary, in the 2D CMK-3, which is the least stable structure, the ion transportation rapidly decreased with addition of Fe_2O_3 nanoparticles. The Z_w of CMK-3-8.1 and CMK-3-19.7 were 5.2Ω and 6.5Ω , which were more than 3 times larger than FDU-15-7.8 and FDU-15-20.0, respectively. This implies significant loss of ion mobility caused by the greatly increased tortuosity in the collapsed CMK-3 structure. In the 3D mesoporous CMK-8 structure, the value of Z_w in CMK-8-7.6 (4.3Ω), CMK-8-21.4 (5.4Ω) and CMK-8-47.1 (6.8Ω) was slightly smaller than in CMK-3/ Fe_2O_3 with similar Fe_2O_3 content, but still much larger than in FDU-15/ Fe_2O_3 composites. This observation is consistent with a moderate tortuosity increase which would be expected from the disruption of the 3D mesoporous network with medium stability.

Figure 3 Nyquist plots (a-c) and Bode plots (d-f) for FDU-15 system (a, d), CMK-3 system (b, e), and CMK-8 system (c, f). The inset of (a) shows the equivalent Randles circuit.

Table 2 EIS parameters for different OMCs & OMC/Fe₂O₃ composites

Sample ID	R_s (Ω)	R_{ct} (Ω)	Z_w (Ω)	τ (s)
FDU-15	2.3	0.6	0.8	0.5
FDU-15-7.8	2.1	0.9	1.4	0.9
FDU-15-20.0	2.0	1.1	2.1	1.2
CMK-3	2.1	1.0	2.5	2.1
CMK-3-8.1	2.2	1.1	5.2	3.7
CMK-3-19.7	2.3	1.3	6.5	4.5
CMK-3-49.9	2.2	1.3	7.6	6.6
CMK-8	2.1	0.9	2.0	1.4
CMK-8-7.6	2.1	1.0	4.3	2.5
CMK-8-21.4	2.3	1.1	5.4	3.0
CMK-8-47.1	2.2	1.3	6.8	3.7

Another important parameter for ion mobility is the dielectric relaxation time constant (τ), which provides a measure for the rate capability and ion transport through a porous electrode. Generally, a small τ means faster ion mobility in the pores. As shown in Figure 3 d-f, τ can be deduced from the Bode plot of the imaginary capacitance, $C''(\omega)$, and the detailed calculation of τ is discussed in the supplemental information [37-39, 46, 47]. The time constant of different mesoporous materials are listed in Table 2. The change of τ can be attributed to R_{ct} and Z_w and reflects conjugation of both parameters. Hence, for same mesostructures, τ will increase with an increase of Fe₂O₃ %. Additionally, the FDU-15 series samples showed the smallest τ less than 1.2 s, even compared with pure hard templated carbon CMK-3 (2.1 s) and CMK-8 (1.4 s), indicating again, that the well preserved 1D channels of FDU-15 facilitate ion mobility. In addition, at similar Fe₂O₃ %, the 3D CMK-8 had a smaller τ than 2D CMK-3, which supports other observations that the 3D structure is more stable than the 2D structure.

3.2.2 Influence of mesostructure on capacitance performance – electrochemical behavior of bare mesoporous carbons.

Figure 4 (a-c) Cyclic Voltammetry curves of (a) FDU-15 and FDU-15/Fe₂O₃ composites, (b) CMK-3 and CMK-3/Fe₂O₃ composites, and (c) CMK-8 and CMK-8/Fe₂O₃ composites in 1M Na₂SO₃ at scan rate of 5mV s⁻¹, (d) Specific capacitances of FDU-15, CMK-3, and CMK-8 at different scan rates.

We first investigated the capacitance performance of bare mesoporous carbons without loading of Fe₂O₃ to study the effect of pore shape on the ion mobility within the pores. The black curves in Figure 4 a-c shows the cyclic voltammetry (CV) of different structured OMCs at scan rate of 5 mV s⁻¹. All of OMCs showed relatively flat, rectangular-shaped CV curves, which are typical for electrochemical double-layer capacitors [48, 49]. Based on the CV curves, the specific capacitances of FDU-15, CMK-3, and CMK-8 at scan rate of 5 mV s⁻¹ are 87, 126, and 113 F g⁻¹, respectively, which is a

trend mostly determined by their total surface area. The corresponding specific capacitances by total surface area are 15.7, 10.0, and 11.4 $\mu\text{F cm}^{-2}$ for FDU-15, CMK-3, and CMK-8, respectively, which are in the same range of the reported OMCs' capacitances [50-55]. The relative area capacitance values of FDU-15 > CMK-8 > CMK-3 are in good agreement with the previous comparison studies between different structured OMCs [51, 52, 56].

Figure 4d present the capacitance of the various OMCs as a function of the scan-rate. Although the capacitance of 1D FDU-15 is smaller than the other two OMCs, the capacitance retention between 5 mV s^{-1} and 200 mV s^{-1} ($C_{200\text{mV}}/C_{5\text{mV}}$) of the FDU-15 (59 %) was higher than CMK-3 (53 %) and CMK-8 (57 %), indicates faster ion mobility in the 1D mesoporous FDU-15, which is in very good agreement with the trends found for Z_w and τ values in the EIS measurements.

3.2.3 Influence of mesostructure stability on capacitance performance – electrochemical behavior of OMC with loading of Fe_2O_3 .

Figure 4 a-c compared the CV curves of OMCs and OMC/ Fe_2O_3 composites. As the Fe_2O_3 % increases, the CV curves gradually deviate from the ideal rectangular shape of EDLCs, mostly due to the broad peaks at ~ -0.3 V and < -0.6 V, which are typical for iron oxide in Na_2SO_3 aqueous electrolyte [27, 57-61] and are due to the redox reactions from sulfite anions adsorbed on Fe_2O_3 and redox reactions between Fe(II) and Fe(III) [58, 61].

The capacitances of three types of mesoporous carbons with various loading amounts of Fe_2O_3 (~ 8 % to ~ 50 %) at different scan rates are presented in Figure 5 a-c. Based on the Fe_2O_3 loading amount and capacitance difference of carbon and carbon/ Fe_2O_3 , the specific capacitance of Fe_2O_3 can be calculated from the following equation:

$$C_{\text{Fe}_2\text{O}_3} = \frac{C_{\text{total}} - C_C \times (1 - \text{Fe}_2\text{O}_3 \%) }{\text{Fe}_2\text{O}_3 \%} \quad (1)$$

In which $C_{\text{Fe}_2\text{O}_3}$, C_C , and C_{total} are specific capacitances of Fe_2O_3 , OMC, and the OMC/ Fe_2O_3 composite, respectively, and Fe_2O_3 % is the mass percentage of Fe_2O_3 in the

OMC/Fe₂O₃ composite. The calculated Fe₂O₃ capacitances as function of loading amount are shown in Figure 5 d-f.

Even with only ~8 % of Fe₂O₃, the electrode gained 30-50 % increase in the total capacitance from the Fe₂O₃ contribution. The demonstrated capacitances attributed to Fe₂O₃ in all of our OMCs, *e.g.*, FDU-15-7.8 (677 F g⁻¹), CMK-8-7.6 (587 F g⁻¹), and CMK-3-8.1 (570 F g⁻¹), were much higher than the values previously reported for Fe₃O₄ nanoparticles (37.9 F g⁻¹ [44] and 174 F g⁻¹ [61]), Fe₃O₄/Fe₂O₃ films (118.2 F g⁻¹ [57] and 210 F g⁻¹ [59]), Fe₃O₄ in CNT/Fe₃O₄ composites (128 F g⁻¹ [62]), and even for mesoporous Fe₂O₃ synthesized by same method but without carbon (173 F g⁻¹, Figure S2). Hence, we demonstrate that loading of Fe₂O₃ into the mesoporous OMCs induced synergic effect in which the conductive carbon scaffold, with free ionic mobility in the mesoporous structure, enabled optimized utilization of Fe₂O₃ capacitance.

Figure 5 Specific capacitance of OMCs and OMC/Fe₂O₃ (a-c), and calculated capacitance of Fe₂O₃ (d-f) with different Fe₂O₃ % at the scan rates of 5 mV s⁻¹, 50 mV s⁻¹, and 200 mV s⁻¹, (a, d) FDU-15 system, (b, e) CMK-3 system, and (c, f) CMK-8 system.

As the specific capacitance of metal oxide is much higher than mesoporous carbon, there is incentive to load as much oxide as possible into the carbon scaffold. However, due to

the small pore volume of FDU-15, the highest possible Fe_2O_3 loading amount is only 20 %. Therefore, only the capacitances of low and medium Fe_2O_3 % are presented in FDU-15/ Fe_2O_3 samples. On the contrary, CMK-8 and CMK-3 benefit from their larger pore volume and can achieve up to ~ 50 % of Fe_2O_3 loading. Our results showed that with the highest Fe_2O_3 loading, the iron oxide enabled 50-90 % increase in the total capacitance of the electrode at slow scan rates. On the other hand, as been reported previously in OMC/ MnO_2 [63] and nitrogen-enriched mesoporous carbons/ RuO_2 systems [64], loading larger amounts of guest metal oxides will decrease the pore volume and may clog the pores, induce formation of larger oxide particles, and hinder the ion mobility and electrolyte penetration into the composite. This is clearly demonstrated in Figure 5 d-f, which show the decreased $C_{\text{Fe}_2\text{O}_3}$ with increasing Fe_2O_3 %, regardless of mesostructure.

Additionally, due to the different structure stability, it is expected that the electrochemical performance of 1D, 2D, and 3D mesostructured OMC/ Fe_2O_3 composites behave differently with increasing Fe_2O_3 %. This is proved by comparing values of $C_{\text{Fe}_2\text{O}_3}$ and rate performances of the composites in different mesostructures.

In the 1D mesoporous FDU-15/ Fe_2O_3 , the capacitances at medium and high scan rates kept increasing with the addition of more Fe_2O_3 (Figure 5a). Regardless of Fe_2O_3 content, the $C_{200\text{mV}}/C_{5\text{mV}}$ was 59%, which is same as pure FDU-15. Even at rate of 200 mV s^{-1} , the calculated Fe_2O_3 capacitance in the highest Fe_2O_3 loaded sample FDU-15-20.0 was 261 F g^{-1} . We attribute this positive trend to the stability of the mesostructure as demonstrated by the TEM and N_2 adsorption–desorption isotherms.

On the contrary, in the commonly used 2D CMK-3 system, as observed in N_2 adsorption–desorption and TEM, most of the mesopores were collapsed before Fe_2O_3 content increased to ~20 %. Zhi *et. al.* [65] reported that in the range of 1.5 nm – 3 nm, decrease in pore size will strongly prohibit the ion accessibility in the mesopores. In CMK-3 samples, the pore diameter dramatically decreased from 3.2 nm in CMK-3 to less than 1.7 nm in CMK-3-19.7. This pore size decreases together with a reduction of pore volume which results in a composite capacitance drop between 12.6 % and 19.7 % under

medium and high scan rates (Figure 5b). The $C_{200\text{mV}}/C_{5\text{mV}}$ of 2D mesoporous composite dropped from 53 % in CMK-3, to 40 % in CMK-3-19.7. The calculated Fe_2O_3 capacitance in CMK-3-19.7 was 190 F g^{-1} and 72 F g^{-1} at 50 mV s^{-1} and 200 mV s^{-1} (Figure 5e), which were only 56% and 27% of the values in FDU-15-20.0 at the same scan rates. This is in agreement with the prohibited ion mobility detected by EIS. Although CMK-3 can load a large amount of Fe_2O_3 , due to the completely collapsed mesopores, the capacitance of CMK-3-49.9 is even smaller than pure CMK-3 at the rate of 200 mV s^{-1} , which results in only 29 % of the $C_{200\text{mV}}/C_{5\text{mV}}$.

In the case of 3D mesoporous CMK-8/ Fe_2O_3 , which has moderate structure stability and ion accessibility, both composite capacitance and calculated Fe_2O_3 capacitance stand between FDU-15/ Fe_2O_3 and CMK-3/ Fe_2O_3 . The CMK-8-21.4 has 179 and 93 F g^{-1} of total capacitance at 5 mV s^{-1} and 200 mV s^{-1} , which results in 52 % of $C_{200\text{mV}}/C_{5\text{mV}}$. Compared with 57 % of $C_{200\text{mV}}/C_{5\text{mV}}$ in CMK-8, the moderate decrease of $C_{200\text{mV}}/C_{5\text{mV}}$ is due to the partially broken 3D porous system. However, as revealed by N_2 adsorption–desorption and TEM, at highest loading of 47.1 %, most of the mesopores have collapsed, resulting in a small pore volume and $< 1.7 \text{ nm}$ pore diameter, which is similar as CMK-3-19.7. Therefore, although CMK-8-47.1 shows 210 F g^{-1} total capacitance at 5 mV s^{-1} , it only preserves 36 % of that capacitance at 200 mV s^{-1} due to the limited ion accessibility.

Figure 6 Cycling performances of FDU-15-20.0, CMK-3-19.7, and CMK-8-21.4 in 1 M Na_2SO_3 solution at current density of 5 A g^{-1} .

The above discussion clearly reveals the correlations between structural stability and rate performance. Beside rate performance, the cycling performance is also expected to be influenced by the structure stability. Here, the cycling stabilities of medium Fe_2O_3 loaded samples were evaluated by galvanostatic charge-discharge method at current density of 5 A g^{-1} . From Figure 6, after 1000 cycles, the capacitance retention of FDU-15-20.0, CMK-8-21.4, and CMK-3-19.7 are 89.8 %, 83.1 %, and 64.8%, respectively, which is in good agreement with their structure stability.

4. Conclusion

Three OMCs with 1D cylindrical, 2D hexagonal, and 3D bicontinuous symmetries were synthesized and used as host materials for OMC/ Fe_2O_3 composites. The influences of mesostructure and structure stability on the ion mobility were systematically characterized, and their effects on capacitance performance were fully studied. Our results show that although the high surface area and pore volume lead to a large carbon capacitance and Fe_2O_3 % in 2D mesoporous CMK-3, the intrinsically unstable mesostructure results in an unfavorable ionic accessibility and bad rate performance. On the other hand, 1D mesoporous FDU-15 from a soft template method has the most stable structure and provides the best structure for ion mobility. Therefore, when loaded with Fe_2O_3 , it has the best rate performance, cycling stability, and Fe_2O_3 specific capacitance. The surface area and stability of the 3D CMK-8/ Fe_2O_3 composites is between the above two materials, so that it can achieve the highest total capacitance at low scan rate. But the unstable mesostructure limited their high rate performance, especially for the high Fe_2O_3 % samples. Clearly, there is a trade-off between ion transportation, mesostructure stability, and structural parameters such as surface area, pore size, and pore volume. In order to get a better electrochemical performance of mesoporous carbon/metal oxide composite, an ideal host material should combine the advantages of both soft template OMCs and hard template OMCs to maximize surface area and pore volume, while also maximizing structural stability and ion access.

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