Improving the capacitive deionisation performance by optimising pore structures of the electrodes

L. Zou, L. Li, H. Song and G. Morris

ABSTRACT

In this paper, three types of ordered mesoporous carbons (OMCs) were synthesised by an original template method and a modified sol-gel process involving nickel salts. The effects of pore arrangement pattern (ordered and random), and pore size distribution (mesoporous and microporous) on the desalination performance were investigated by comparing mesoporous carbons with activated carbons (ACs). It is found that the mesoporous carbons prepared by addition of nickel salts demonstrated higher specific capacitances than mesoporous carbons without nickel salts and the activated carbon electrodes. Their electrosorptive deionisation properties were also compared in a dilute NaCl solution (conductivity $100\,\mu S\,cm^{-1}$), the amount of adsorbed ions are measured by a flow though apparatus in the laboratory. It is found that the amounts of the adsorbed ions are $15.9\,\mu mol\,g^{-1}$ for OMCs involving nickel in the synthesis process, $10.3\,\mu mol\,g^{-1}$ for OMC not involving nickel salts and $4.7\,\mu mol\,g^{-1}$ for ACs.

Key words | activated carbons, capacitive deionisation, electrosorption, mesoporous carbon electrodes

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INTRODUCTION

Research on developing an economical, efficient alternative desalination technology is vital for the sustainable future of clean water supplies worldwide. The overwhelming majority of desalination technology uses membranes, and although recent advancements have reduced the cost of membranes, its operation still requires high-energy and a great deal of maintenance. An alternative technology, capacitive deionisation (CDI) or called as electrosorption, uses porous carbon electrodes and operates at low voltage, and is therefore a low energy-demand process (Farmer *et al.* 1996*a,b*, 1997). This research aims to improve the performance of electrosorption desalination by evaluating the porous carbon materials that have superior properties for electrosorption and desorption in terms of their pore structure, morphology and electrochemical properties.

The CDI energy consumption comprises two components, i.e. electrical charge potential applied across the electrodes, and pump energy consumption to drive the fluid

through. As this article reports a bench scale CDI cell, the main focus of this research is to compare the differences of each type of electrode materials, it is found that the energy used for the electrical charge potential is very low, compared to the pumping energy consumption. The energy consumption reported in the literature is used here. Lawrence Livermore National Laboratory (Farmer *et al.* 1997) has calculated the energy required of using carbon aerogel as electrode in electrosorption for desalination. For an electrode with a separation distance of 0.035 cm, the electrosorption cell required $0.14\text{–}0.28\,kWh/m^3$ $(0.50\text{–}1.01\,kJ/L)$.

Electrode materials for CDI have been developed to a great extent in the previous research. However, ways have yet to be found for increasing the practically available surface area for ion electrosorption and desorption. This should certainly be considered in the light of careful design of the pore structure and pore frameworks. At present, the

carbon electrodes used in CDI research and development such as carbon aerogel and various forms of activated carbons, have a high surface area, but their electrosorption capacity is limited. This is due to their non-ideal pore structure, as they contain randomly connected pores and their pore sizes are widely distributed. To overcome this deficiency, carbon materials with good electrical conductivity and large and especially more accessible surface areas are required. It is therefore imperative to develop advanced carbon materials such as ordered mesoporous carbons (OMCs) which have both high surface areas and controlled pores structure that is ideal for better salt ion adsorption and desorption. Further investigation is needed to confirm the effects of using ordered mesoporous carbons as electrode materials, especially on if their interconnected pore network can facilitate efficient electrosorption and desorption; and if the meso-ranged pore size is large enough to be completely accessed by the ions and also be small enough to result in a large surface area.

In this paper, three types of ordered mesoporous carbons (OMCs) were synthesised by an original template method and a modified sol-gel process involving nickel salts. The effects of pore arrangement pattern (ordered and random), and pore size distribution (mesoporous and microporous) on the desalination performance was investigated by comparing mesoporous carbons with activated carbons (ACs). It is anticipated that the other carbon types available commercially will have a similar results in desalination to activated carbons shown in this research, none of the reported carbons can achieve the high performance of OMCs as reported in this paper.

METHODS

Preparation of mesoporous carbon electrodes

OMCs were prepared by a soft template method as reported in the literature (Ryoo *et al.* 1999; Lee *et al.* 2002; Kim *et al.* 2004; Li *et al.* 2006a,b; Zou *et al.* 2008). Typical preparations use precursors including triblock copolymer P123, tetraecethyl orthosilicate (TEOS) and sulphuric acid, in a hydrothermal process to obtain as-synthesis product. The product will then be calcinated in a furnace, followed

by removal of the silica template. The detailed process was as follows: (1) 5 g of triblock copolymer P123 (Aldrich) was dissolved in the solution composed of 130 ml of de-ionized water and 6.36 ml of sulphuric acid at 313 K. After 3 h, 9.2 ml of tetraethyl orthosilicate (TEOS) was added to the above solution under stirring, and the resulting solution was aged at 313 K for 24 h, followed by further aging at 373 K for 36 h. The resultant precipitate was filtered, washed and dried at room temperature to obtain an as-synthesized composite; (2) the as-synthesized composite was dried in a drying oven at 373 K for 6 h and 433 K for 6 h, respectively; (3) the resultant dark brown material was carbonized in a horizontal furnace under pure nitrogen atmosphere at 1,123 K for 2 h for the complete carbonization of P123; (4) the resulting carbon/silica composite was immersed in 48% hydrofluoric acid at room temperature for 24 h to remove the silica template; (5) the carbon material obtained as an insoluble fraction was repeatedly washed with de-ionized water and then dried in air at 373 K. The second route involves using a nickel salt at the beginning of the OMC synthesis. This modification will result in higher BET surface areas and more controlled pore size.

The second route involves using a nickel salts at the beginning of the OMC synthesis. This modification will result in higher BET surface areas and more controlled pore size. The products prepared by the addition of $NiSO_4 \cdot 6H_2O$ and $Ni (NO_3)_2 \cdot 6H_2O$ are denoted as OMC-S and OMC-N, respectively, where S and N indicate the kind of nickel salt used. To investigate the effect of nickel salt on the resultant carbon material, an ordered mesoporous carbon without the use of nickel salt was prepared and is denoted as OMC-W, where W represents the absence of nickel salt.

Characterisation of the porous carbon electrodes

All the synthesised carbon materials were characterised by small angle X-ray scattering spectrometer (SAXS), transmission electron microscopy (TEM) and N_2 adsorption–desorption BET and BJH surface and pore size/volume analyser. SAXs patterns were collected on a Bruker Nanostar using Cu Kα radiation at 40 kV and 40 mA. Each sample was scanned over the q range of 0.1 to 3.0 nm^{-1}. A Hitachi H-800

electron microscope was used for TEM analysis. Nitrogen adsorption-desorption isotherms were performed with a Miromeritics Tristar 3,000 analyser at 77 K. The nickel loading of the silica/carbon/nickel composite was determined by the flame atomic absorption on a GBC 906 AA spectrometer. The air-acetylene flame and the standard method were used.

Electrochemical properties of the porous carbon electrodes

The cyclic voltammetry (CV) analyses were conducted to study the electrochcemical properties using an Autolab/PGSTAT100 potentiostat (Eco Chemie, the Netherlands) with a three-electrode cell. The porous carbon materials were used to prepare the working electrode by pressing a mixture of carbon, graphite and polytetrafluoroethylene (PTFE) on to the graphite sheet which is served as a current collector. The 0.1 M NaCl solution was used as electrolyte solution. The capacitances were calculated from CV curves using the following formula:

$$C = (q_a + |q_c|)/\Delta V \tag{1}$$

where C is the capacitance, q_a and q_c are the anode and cathdic volumetric charges on positive and negative sweeps, repectively, and ΔV is the potential range.

Desalination experiments

A flow through capacitive deionisation unit was designed and built as shown in Figure 1. The unit consists of a pair of cathode and anode made from the porous carbon materials. The experiments were conducted by applying a direct voltage of 0.8 V between the two electrodes. In each experiment, the NaCl solution was continuously pumped from a peristaltic pump into the unit cell and the effluent
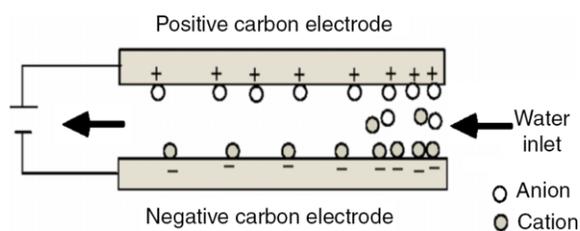

Figure 1 | Schematic of the electrosorption unit cell.

was returned to the cell. Wherein the solution temperature was kept at 298 K, a flow rate of around $20\,\text{ml}\,\text{min}^{-1}$ was maintained, and a total solution volume of 100 ml and an electrode mass of 1.2 g were applied. At the end of the experiment, the applied voltage was removed and as result the adsorbed ions desorbed from the electrodes and the electrodes were regenerated.

By removing the voltage the adsorbed ions came out to achieve the regeneration of electrodes. The concentration changes of NaCl solution were continuously monitored and measured at the outlet of the unit cell using a conductivity metre. NaCl adsorption capacity is calculated according to

$$\eta = (C_0 - C)V/m \times 100\% \tag{2}$$

where C_0 is the starting NaCl concentration, C is the final NaCl concentration, V is the volume of the NaCl solution, and m is the mass of active component in the working electrode.

RESULTS AND DISCUSSIONS

Comparison of the pore structures

The pore arrangement information of the OMCs and AC were obtained by SAXS and TEM and shown in Figure 2 and Figure 3. For the OMC material the appearance of visible peaks in the region of less than 2 degree confirms the
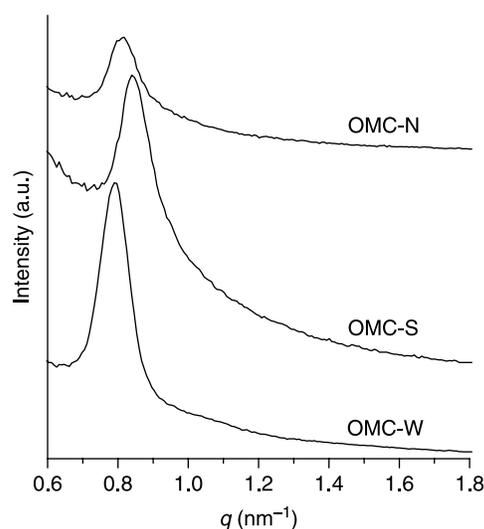

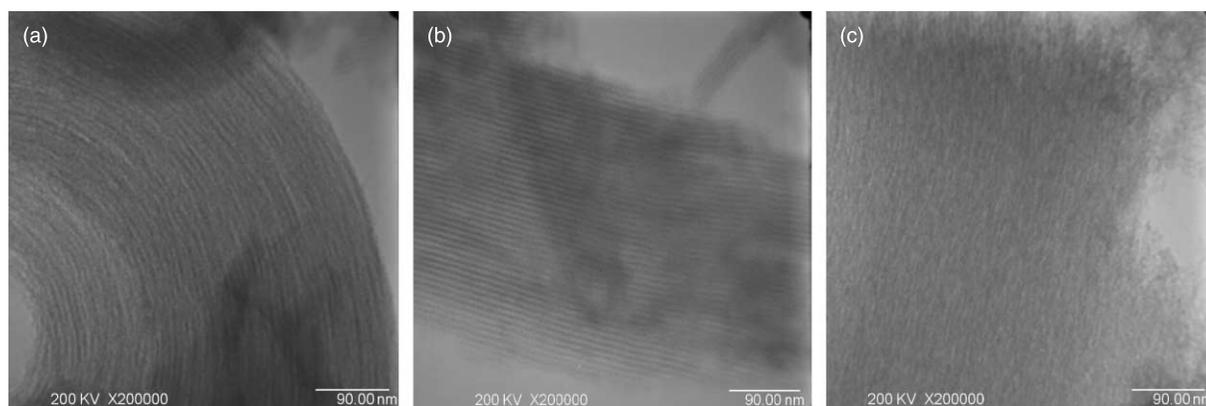**Figure 2** | SAXS patterns of OMCs materials.

Figure 3 │ TEM images of (a) OMC-W, (b) OMC-S and (c) OMC-N.

formation of ordered hexagonal P6mm mesoporous structures (Zhao *et al.* 1998). A strong and narrow peak is observed at the q value of $0.79\,nm^{-1}$ for OMC-W prepared in the absence of metal salt. Although higher order peaks can not be clearly discerned, it is still deduced that its pores are arranged according to P6mm hexagonal structure. In comparison with OMC-W, the SAXS pattern of OMC-S prepared by the addition of $NiSO_4 \cdot 6H_2O$ shows a similar reflection at the q value of $0.83\,nm^{-1}$, whereas only a broad peak with low intensity appears in the case of OMC-N prepared by the addition of $Ni(NO_3)_2 \cdot 6H_2O$, implying that the ordering of the latter on the mesoscopic scale is low. The different effect of two nickel salts on the degree of mesoscopic order should be caused from their different decomposition temperatures during the carbonization process. The TEM images showed in Figure 3 confirm that after the addition of nickel salt into the synthesis, the ordered porous texture is maintained.

The surface area, pore size distribution and pore volumes were determined by using N_2 adsorption-desorption isotherm of the OMC materials. It is clearly observed that all the isotherms are in the shape of irreversible type IV as defined by IUPAC, which is a characteristic feature of the mesoporous solids. Basically the sharpness of the capillary condensation steps indicates the uniformity of mesopore size distribution (Kumar *et al.* 2001). As can be seen from the isotherms, the steps appear in the wide $P/P0$ range of 0.4–0.9, indicating that their mesopores are not perfectly uniform, especially for OMC-W (see Figure 2b). On the other hand, a visible increase of adsorption amount at $P/P0 > 0.9$ could be resulted from

the existence of interparticle pores. It is further deduced from Figure 4b that the mesopore sizes of OMC-S and OMC-N prepared by the addition of nickel salt are slightly smaller than those of OMC-W prepared in the absence of nickel salt, centred at 3.7, 3.3 nm and 4.0 nm, respectively. It is found that the addition of metal ions lead to mesoporous silica materials with reduced pore wall and in turn the carbon replicas with reduced pore size. Compared with OMC-N, the mesopore size of OMC-S is a bit larger due to the different amounts of deposited Ni in silica/carbon/metal composites (5.9 wt.% for OMC-N and 4.1 wt.% for OMC-S). Table 1 summarizes the textural characteristics of these OMC materials. The physical properties of OMC-S and OMC-N prepared by the addition of nickel salt are comparable, such as their BET surface areas reach $1491\,m^2\,g^{-1}$ and $1594\,m^2\,g^{-1}$, respectively, while OMC-W prepared in the absence of nickel salt has a low BET surface area and total pore volume, $950\,m^3\,g^{-1}$ and $1.102\,m^3\,g^{-1}$, respectively. This should be a result of the contribution of nickel nanoparticles.

Comparison of electrochemical properties

Cyclic voltammetry (CV) was used to evaluate the potential possibility of materials used for capacitive deionization, the electrochemical properties such as specific capacitances were obtained for this purpose. The cyclic voltammograms of OMCs and AC swept at a sweep rate of $1\,mV\,s^{-1}$ in 0.1 M NaCl solution are shown in Figure 5. As can be observed, all the CV curves present the typical capacitor-like characteristics with "box-like" shape in the applied
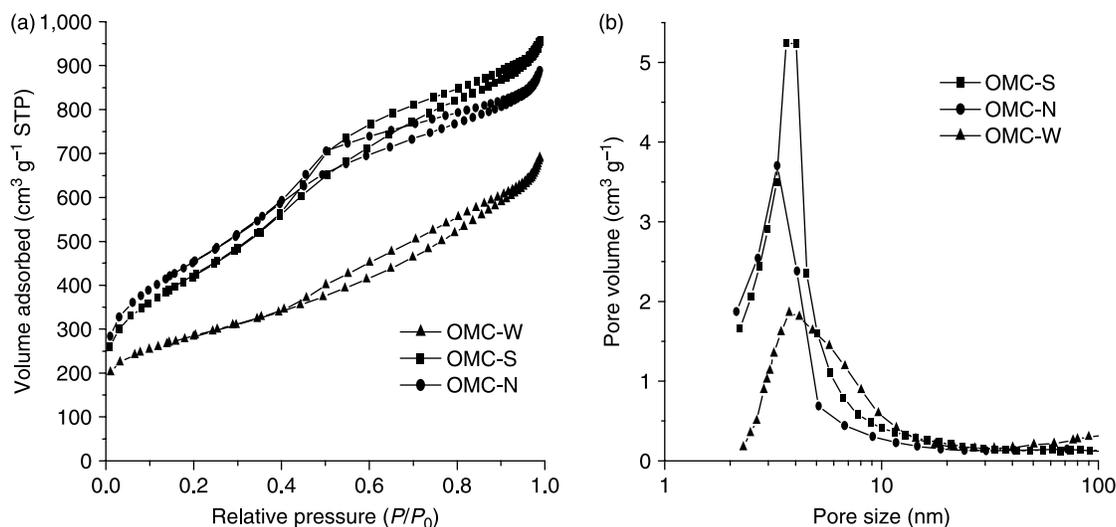
Figure 4 │ (a) Nitrogen adsorption-desorption isotherms, (b) pore size distributions of OMCs.

potential range of $-0.2\,V$–$0.8\,V$. This means that all charge/discharge processes are stable and highly reversible. Thus, the Na^+ and Cl^- ions are removed from the solution by the formed electric double layers and the electrodes can be regenerated. On the other hand, in the case of OMC-S prepared by the addition of $NiSO_4 \cdot 6H_2O$ both cathodic and anodic currents reach higher values than other three carbon materials. Its high BET surface area may play an essential role whereas the ordered mesopores of 3.7 nm are suitable for the transportation of ions. Thus the higher capacitances can be achieved for OMC-S.

The specific capacitances of the carbon electrodes were calculated based on Equation (1). When the sweep rate of $1\,mV\,s^{-1}$ is used, OMC-S and OMC-N achieve the specific capacitances of $192\,F\,g^{-1}$ and $174\,F\,g^{-1}$, respectively, whereas for OMC-W and AC the values are only 140 and $108\,F\,g^{-1}$, respectively. This implies that when nickel salt is added into the synthesis, the more pore surfaces of carbon

electrode are available, the more electrical double layers are formed and thus the desalination efficiency is improved.

Comparison of the desalting capacities

The desalting experiments using OMCs as capacitive electrodes were conducted with a NaCl solution that has an initial concentration of 0.0008 M NaCl (conductivity $100\,\mu S\,cm^{-1}$). During charging, the amplitude of the applied voltage is 0.8 voltage. Figure 6(a) shows the adsorption of NaCl on OMCs and AC. The lower conductivity
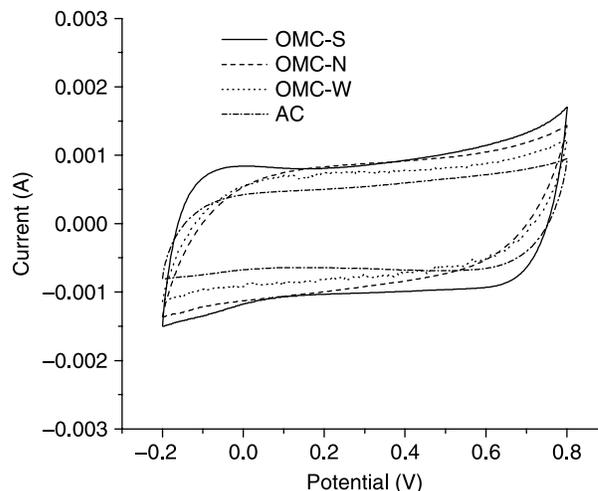
Table 1 │ The textural characteristics of OMCs and a commercial activated carbon

Sample	S_{BET} ($m^2\,g^{-1}$)	S_{mi} ($m^2\,g^{-1}$)	V_t ($m^3\,g^{-1}$)	V_{mi} ($m^3\,g^{-1}$)	D_{me} (nm)
OMC-S	1,491	206	1.589	0.202	3.7
OMC-N	1,594	277	1.453	0.207	3.3
OMC-W	950	298	1.102	0.238	4.0
Activated carbon	845	579	0.605	0.247	

Figure 5 │ Cyclic voltammograms of OMCs and AC swept at $1\,mV\,s^{-1}$ in 0.1 M NaCl solution.
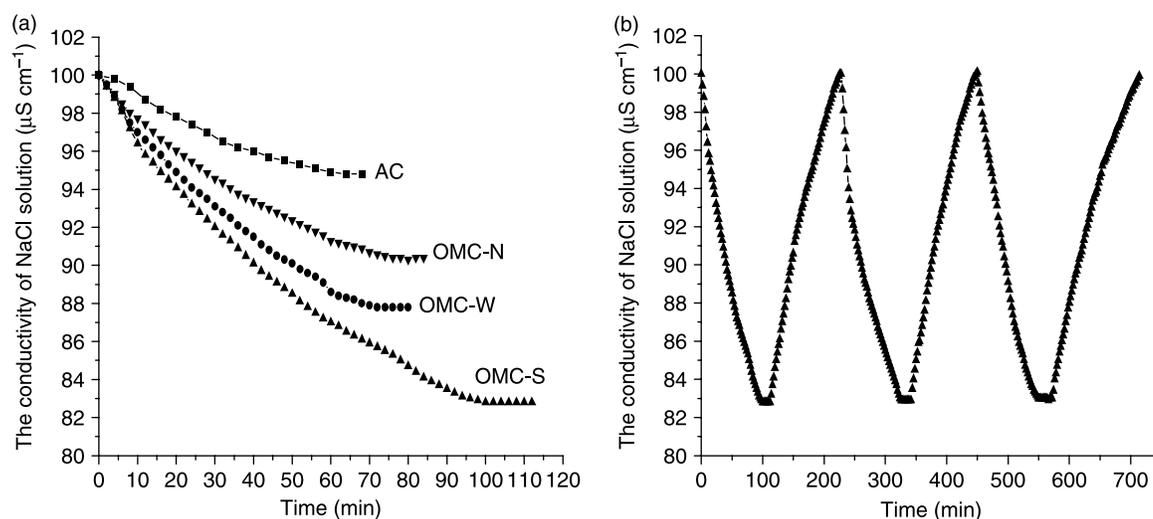
Figure 6 │ (a) Capacitive deionisation of NaCl, (b) Adsorption and desorption of NaCl by OMCs.

value indicates that more ions are adsorbed by the electrodes, i.e. the higher deionisation efficiency is achieved. It is calculated that the amounts of the adsorbed ions calculated using Equation (2) are $15.9\,\mu\mathrm{mol\,g^{-1}}$ for OMC-S, $9.2\,\mu\mathrm{mol\,g^{-1}}$ for OMC-N, $10.3\,\mu\mathrm{mol\,g^{-1}}$ for OMC-W and $4.7\,\mu\mathrm{mol\,g^{-1}}$ for AC. Evidently, OMCs bring about more ions onto the surfaces of electrodes compared with AC. On the other hand, it is necessary to mention that OMC-N shows somewhat lower NaCl adsorption capability than OMC-W. Compared to OMC-W, although OMC-N has higher BET surface areas, it has two other properties i.e. less ordering of its pore structure (Figure 3) and smaller average pore size (Figure 4(b)), that do not favour salt ion adsorption and desorption. It seems to mean that ordered pore structure is more beneficial than BET surface area to the transportation of ions.

Additionally, the ability to be regenerated is very important to the electrodes. Figure 6(b) shows the characteristics of NaCl adsorption and regeneration of OMC-S. After removing voltage the ions of OMC-S electrode are clearly released and thus the process of regeneration could be carried out. As the reported research results is based on the bench scale tests in the laboratory, so it does not considered the background organic matter (BOM) fouling effect on the electrodes. But it is understood that the CDI is a flow through system, the pressure of the system is very low, i.e. 1 atm, as a result of this low pressure, and the biofouling

caused by dissolved organics is less permanent and more reversible. Some of the early commercial models of the CDI use citric acid as a mild cleaning agent, the loosely absorbed BOM can be removed by the regular cleaning by citric acid. So it does not need to use the harsh chemical such as chlorine or sodium perchlorate for cleaning.

CONCLUSIONS

The mesoporous carbons were synthesised by a modified route with the addition of nickel salts into the silica template. Here it has been demonstrated that the carbon synthesis is feasible by mesostructure-directing effect of the metal complexes formed via the interaction of metal ions with the -O- groups of the copolymers. The resultant carbons had higher BET surface areas and smaller ordered mesopores in comparison with ordered mesoporous carbons without the use of nickel salts. It is found that the mesoporous carbons prepared by addition nickel salts demonstrated higher specific capacitance than mesoporous carbons without nickel salts and the activated carbon electrodes. In addition, their electrosorption desalination results show that OMC-S prepared by the addition of $NiSO_4 \cdot 6H_2O$ exhibited maximum capacity in removal of NaCl due to its high BET surface area of $1491\,\mathrm{m^2\,g^{-1}}$ and ordered mesopores of $3.7\,\mathrm{nm}$. The regeneration of the electrodes was confirmed involving desorption of NaCl when the charge is removed.

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