

# SYNTHESIS TiO<sub>2</sub>-CARBON AEROGEL THROUGH SOL-GEL POLYMERIZATION AND APPLICATION IN ELECTROCHEMISTRY

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## Introduction

Carbon aerogel (CA) is a most promising material as an electrode for electrical double-layer capacitor (EDLC), as it allows an interconnected three-dimensional network structure, a high specific surface area, good electrical conductivity and a suitable pore size distribution for common electrolytes. Moreno-Castilla et al.<sup>[1]</sup> prepared titania/carbon composite by the sol-gel method, it has been demonstrated that development of the meso- and macroporosity as well as the surface area in the composite aerogels. According to the reference, TiO<sub>2</sub>-doped carbon aerogel can change pore structure of aerogel. It is expected that this effect would be a potential material for EDLC. Min-Woong Ryoo et al.<sup>[2-3]</sup> studied the role of titania incorporated on activated carbon cloth for capacitive deionization (CDI) of NaCl solution. The incorporated titania on carbon close worked as electrosorption sites of ions, resulting in a significant increase in electrosorption with a considerable decrease in physical adsorption.

The objective of this work is to develop optimum methods for preparation of carbon aerogel in which well dispersed fine TiO<sub>2</sub> particles. Carbon aerogel electrodes applicable to the CDI process on NaCl solution were examined.

## Experimental

Resorcinol(R) and formaldehyde (F) were dissolved in ethanol (E) with a molar ratio of 1:2. TBTi dissolved in ethanol was added drop by drop to the above solution, which was kept a certain temperature with continuous magnetic stirring. The wet sample was dried for some days at 70°C and was washed with acetone until the water was completely exchanged and then dried with supercritical petroleum ether. Carbonization of the TiO<sub>2</sub>-doped organic aerogels was performed at 900 °C for 2h under a N<sub>2</sub> atmosphere. The sample was marked as CA1, compared with the CA0 (blank sample). The carbon electrode was prepared by mixing the carbon aerogel with acetylene carbon black and polytetrafluoroethylene in a weight ratio of 75:20:5, the powder was dissolved in isopropanol. These pastes were uniformly coated on the nickel foam. Then the bead machine was used for compaction. These electrodes were used for electrochemical properties research and capacitive deionization research.

Surface area and pore volume analysis were performed on Thermo Sorp Tomatic 1990. X-ray diffraction patterns for the aerogel powders were obtained with D/Max 2500 diffractometer (40kV and 200mA) using Cu K $\alpha$  radiation. Transmission electron microscopy of TiO<sub>2</sub>-doped carbon aerogels was performed on an H-800 instrument operating at 200 keV. A unit cell for capacitor was fabricated with two electrodes separated by a thin polymer in 30% KOH aqueous solution as electrolyte. Cyclic voltammetry (CV) experiment was realized by using an electrochemical station (Zahner-Elektrok, Germany) in the potential range 0–1.0V. Electrochemical impedance spectroscopy (EIS) measurements were taken at ambient temperature in a frequency range of 100 kHz and 10 mHz by using a frequency response analyzer (Zahner-Elektrok, Germany).

## Results and Discussion

The results of BET surface areas, total pore volume and pore size are presented in Table 1. Compared to the mesopore volume, total pore volume and the average pore sizes, the sample of CA1 increased about 95%, 188% and 176%. For these fine powders, it is increased by TiO<sub>2</sub> addition.

The XRD patterns of samples CA0 and CA1, depicted in Fig.1. Sample CA0 shows 2 peaks at around 23° and 43.5°, corresponding to (002) and (100) graphite diffraction peaks. The (100) diffraction peak is narrower in samples CA1 than in samples CA0, which indicates that metal ion can catalyze the partial graphitization of the carbon aerogel structure. Sample CA1 was apart from the carbon peak in addition to titanium peak by only the anatase phase. Anatase is a metastable polymorphic form of titania and transforms to rutile upon heating.

Table 1 Surface area and porosity analysis of CAs

Sample	S <sub>BET</sub> m <sup>2</sup> /g	Mesopore volume cm <sup>3</sup> /g	Pore volume cm <sup>3</sup> /g	D nm
CA0	502	0.39	0.48	3.8
CA1	528	0.76	1.38	10.5

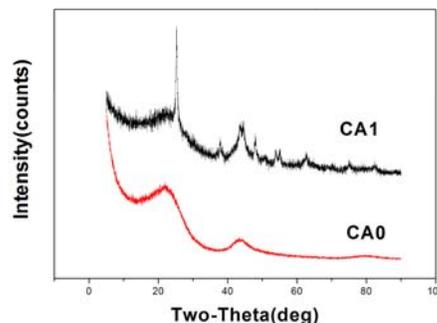


Fig.1 XRD patterns of sample CA0 and CA1

Titania dispersion in CA samples was analyzed by TEM. TEM image of the sample CA1 shown in Fig. 2 indicates that

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the distribution of the titania nanoparticles is very homogeneous and the average particle size of the titania is about 20 nm.

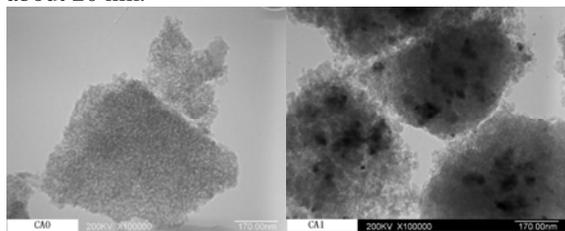


Fig.2 TEM images of CA0, CA1.

The cyclic voltammogram curves of CA1 sample were recorded at room temperature in 30% KOH aqueous solution at a potential range of 0–1V at scan rate of 1mV/s are shown in Fig.3. No significant Faradaic reaction was observed during the experiment, so the cyclic voltammetry behaviour represented primarily the EDLC caused by electrostatic attractive force of the carbon aerogel electrodes. The reason for this is probably because the titania in the structure did not take part in redox reactions. The Nyquist plot obtained for sample CA1 are shown in Fig. 4. In the end of semi-circle arc, a straight line with a slope of 45° from the real axis is observed that corresponds to semi-infinite Warburg impedance, which shows ion penetration in the thickness of the porous structure of the electrode. It can be seen that the Warburg impedance shows lower resistance, which is due to the sample of CA1 have large numbers of mesopore, result in the ion easy penetrate to the porous structure of the electrode. In low frequency region, all the plots are nearly vertical lines, which demonstrated a pure capacitance characteristic.

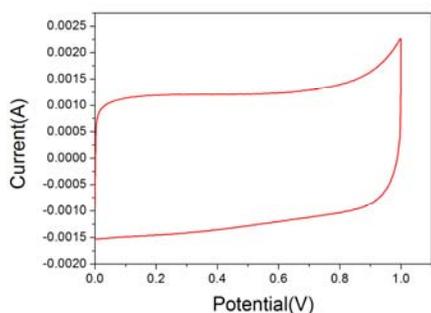


Fig.3 Cyclic voltammograms of CA1 sample measured at 1mV/s in 30% KOH aqueous solution

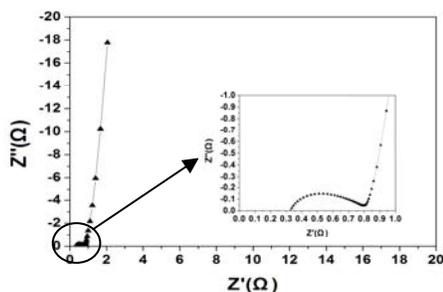


Fig. 4 Electrochemical impedance plot for sample CA1 in 30% KOH

The desalting efficiency was performed with 50 mL of the 2000 mg/L NaCl solution through a CDI unit cell with carbon aerogel electrode. The applied voltage was 1.5 V and the flow rate was 10mL/min. Fig.5 shows adsorption of ions on the CA0 and CA1 electrodes with physical adsorption and electrosorption. It can be seen that physical adsorptions of ions on the CA0 electrode was hugely larger than that on the CA1 electrode. However, electrosorption was contrary. The electrosorption amount of CA1 is 10.7mg/g to 4.5 times for CA0 (2.4 mg/g). It can be believed that the TiO<sub>2</sub>-carbon aerogel is an excellent material when it used as electrode material in capacitive deionization.

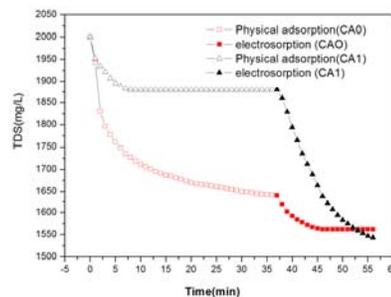


Fig.5 Adsorption of NaCl on the CA0 and CA1 electrodes at applied voltages of 1.5V

## Conclusions

TiO<sub>2</sub>-doped carbon aerogels were prepared by sol-gel synthetic method and supercritical drying process. The added titania significantly increases the average pore size and pore volume. XRD shows the crystallinity of the particles is anatase phase and incorporated titania can catalyze the partial graphitization of the carbon aerogel structure.

TiO<sub>2</sub>-doped carbon aerogels had stable electrochemical properties and little internal resistance, they are considered as promising materials for supercapacitors. From the CDI process on NaCl solution, the incorporation of titania on CA is effective for the considerable enhancement of its CDI performance and decrease its physical adsorption.

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## References

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