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Short communication

Nano zirconium oxide/carbon black as a new electrode material for electrochemical double layer capacitors

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ABSTRACT

In this paper, nano ZrO_2/carbon black was evaluated as a possible electrode candidate material for electrochemical capacitors. Mechanical pressing as a fast and easy method was used for electrode fabrication. Regarding the utility in supercapacitors, the electrochemical properties of the produced nanocomposite was studied using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests in 2 M KCl, KOH and $NaNO_3$ electrolytes. Scanning electron microscopy (SEM) was used to characterize the microstructure and nature of the nanocomposite produced. The results obtained show that the 30:60:10 (carbon black:ZrO_2:polytetrafluoroethylene) type electrode has a specific capacitance as high as 43.20 F g^{-1}, in the potential range of −0.15 to 0.55 V (vs. SCE) in 2 M KCl at scan rate of 10 mV s^{-1}. SEM images confirm the porous structure of ZrO_2/carbon black nanocomposite electrode. Also, charge/discharge cycling test shows a good reversibility and confirms that the electrical resistance would increase after 100 cycles.

1. Introduction

Electrochemical capacitors store the electric energy in an electrochemical double layer (Helmholtz Layer) formed at a solid/electrolyte interface. Positive and negative ionic charges within the electrolyte accumulate at the surface of the solid electrode and compensate the electronic charge at the electrode surface [1]. High cycle life, more than 500,000 cycles at 100% depth of discharge, and high lifetime, up to 12 years, high energy efficiency ranging from 85% up to 98% and high self-discharge rate are some of the supercapacitors characteristics [2].

Depending on the charge-storage mechanisms, capacitors can be classified in three types: Electrochemical double layer capacitors (EDLC), faradic pseudocapacitors and hybrid capacitors [3,4]. EDLCs store the electric charge directly across the DL of the electrode [3]. Since no chemical action is involved, the effect is easily reversible with minimal degradation in deep discharge or overcharge and the typical life cycle is hundreds of thousands of cycles [5].

With respect to electrode materials there are three main categories: carbon-based, transition metal oxides, and conductive polymers [3]. Transition metal oxides are considered to be the most suitable candidate materials for EC. This stems from the high specific capacitance coupled with very low resistance resulting in a high specific power which makes them suitable for commercial applications.

In this paper, mechanical pressing as a fast and easy method was used to fabricate nano ZrO_2/carbon black electrode. The product was evaluated as a possible candidate electrode material for electrochemical capacitors using different techniques including cyclic voltammetry, electrochemical impedance spectroscopy and scanning electron microscopy.

2. Experimental

2.1. Materials

High purity (>99%) nano zirconium oxide (<100 nm), nickel foil (99.99% with 0.125 mm thickness) and polytetrafluoroethylene (<2 μm) were purchased from Aldrich. All other chemicals used in this study were purchased from Merck. The mixture containing different wt% ZrO_2 and carbon black (CB) and 10 wt% polytetrafluoroethylene (PTFE) was well mixed in ethanol to form a paste and then was pressed onto nickel foil (4×10^7 Pa) which served as a current collector (surface was 0.785 cm^2). The typical mass load of electrode material was 30 mg. The used electrolytes were 2 M KCl, NaCl and $NaNO_3$.

2.2. Characterization

The electrochemical behavior of ZrO_2/CB nanocomposite was characterized using CV and EIS tests. The electrochemical

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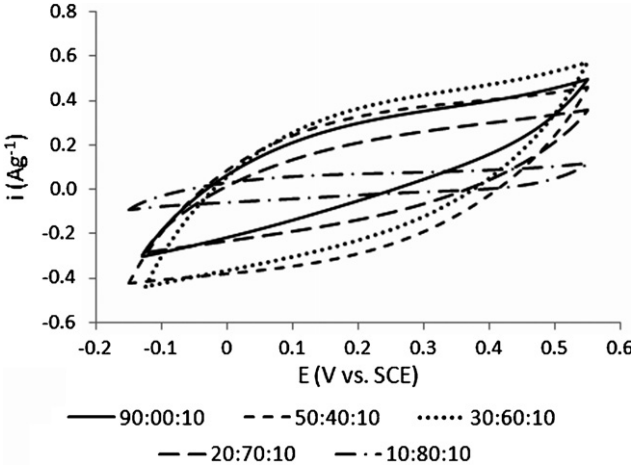

Fig. 1. CV curves obtained from different nano ZrO_2-content electrodes in 2 M KCl at 10 mV s^{-1}.

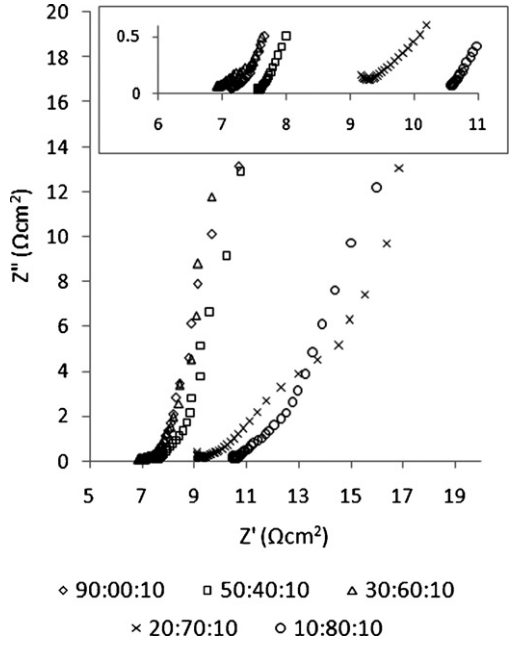

Fig. 2. Nyquist diagrams of different ZrO_2-content electrodes in 2 M KCl electrolyte.

measurements were performed using an Autolab (Netherlands) Model PGSTAT 302 N. CV tests were performed within the range of −0.15 and +0.55 V (vs. SCE), using scan rates of 10, 20, 30, 50 and 100 mV s^{-1}. EIS measurements were also carried out in the frequency range of 100 kHz to 0.01 Hz at open circuit potential with ac amplitude of 10 mV. The specific capacitance C (F g^{-1}) of the active material was determined by integrating either the oxidative or the reductive parts of the cyclic voltammogram curve to obtain the voltammetric charge Q (C). This charge was subsequently divided by the mass of active material m (g) in the electrode and the width of the potential window of the cyclic voltammogram ΔE (V), i.e., $C = Q/(\Delta E m)$ [3]. The morphology and nature of the porous electrode were studied using scanning electron microscopy (TESCAN, USA).

3. Results and discussion

Fig. 1 shows the second CVs of different ZrO_2-containing electrodes (carbon black:ZrO_2:polytetrafluoroethylene) at scan rate of 10 mV s^{-1} in 2 M KCl electrolyte. CVs exhibit a rectangular shaped profile, which is characteristic of ideal capacitive behavior [6]. All of these electrodes exhibited almost potential-independent double-layer capacitance, over appreciable ranges of polarization voltage. As the ZrO_2 content increases (below 60%), the electrode current peak increases as well. The initial reason could be the increasing of specific surface area. However, as the nano content increases (above 60%) current peak decreases and causes to lower the calculated capacitance. This current peak reduction may be due to increasing the electrode resistance (Fig. 2). As shown in Fig. 2, the point of intersecting with the real axis of Nyquist curves in the range of high frequency is the equivalent series resistance (ESR). It indicates the total resistance of the electrode, the bulk electrolyte resistance and the resistance at electrolyte/electrode interface [3]. Therefore, two counter acting parameters will act simultaneously as the nano ZrO_2 content increases: increasing the specific surface area and decreasing the electrode conductivity. It is concluded that 30-60-10 electrode have as high as 43.20 F g^{-1} capacitance in 2 M KCl electrolyte. So, this electrode was selected for further investigation: i.e. effect of electrolyte, scan rate and charge–discharge cycles.

2 M KCl, 2 M $NaNO_3$ and 2 M KOH were investigated as electrolyte at scan rate of 10 mV s^{-1} (Fig. 3). Ideal capacitative behavior was observed in the cases of KCl and $NaNO_3$ electrolytes. In the case of KCl and KOH, although the cation ions of the electrolyte are the same but the specific capacitance in 2 M KCl is as high as 43.20 F g^{-1} compared with the basic electrolyte that shows no ideal capacitance behavior. Ion size and diffusion of anions and cations are important parameters for specific capacitance calculation. When the KCl and KOH electrolytes are compared, the pronounced difference is the anion nature. Since the hydroxyl ion is bigger than the

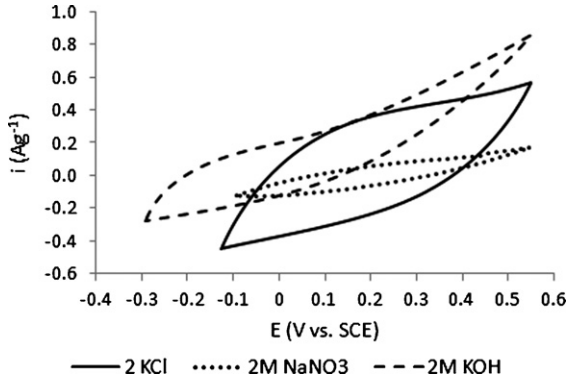

Fig. 3. CV curves obtained from 30:60:10 electrode in different electrolytes at 10 mV s^{-1}.

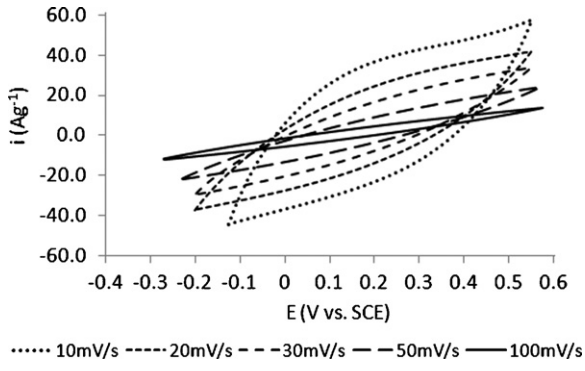

Fig. 4. CV curves obtained from different scan rates of 30:60:10 type electrode.

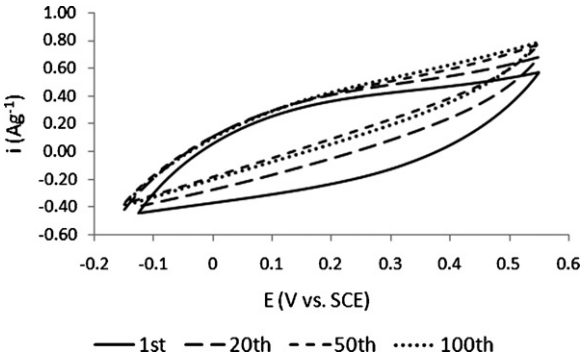

Fig. 5. Representative cyclic voltammograms obtained from 30:60:10 type electrode at 10 mV s^{-1}.

chloride ion, potassium ions might be hindered by bigger hydroxyl ions, which lead to non-capacitive behavior. Comparison of KCl and $NaNO_3$ confirms that the high ionic radius of anions is an important parameter for capacitance behavior. At the same scan rates, high ionic radius of nitrate ions limits the diffusion and the movement of Na^+ and NO^{3-} ions into the surface pores and only the outer active surface is utilized for the charge storage. This leads to low specific capacitance of 10.82 F g^{-1} obtained from 2 M $NaNO_3$ electrolyte. However, at lower scan rates, all the active surface area can be utilized for charge storage.

As the scan rate increases (Fig. 4) the current versus potential relation of CV would deviate from the classical square waveform, expected for a pure capacitor. As discussed by some researchers this is due to the resistance effects down the pores [7]. In addition to pore resistance, efficiency is another important parameter affecting the capacitance in high sweep rates. As the sweep rate increases, loss of energy increases and the stored charge on the electrode surface decreases causing the capacitance to decrease (Fig. 4).

The cyclic stability of supercapacitors is a crucial parameter for their practical applications. As for pseudo-capacitive materials, the life cycle of both conducting polymers and metal oxides is much

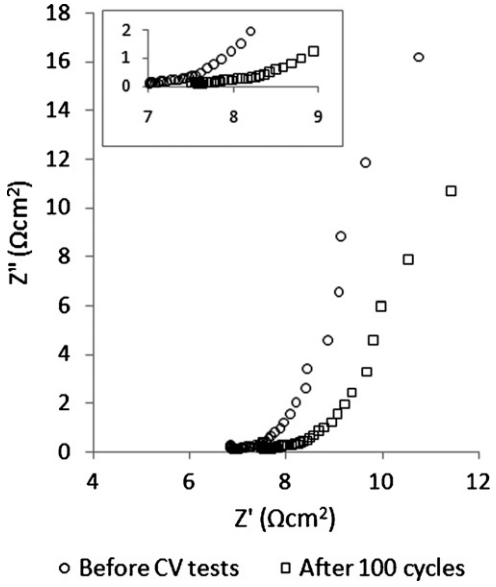

Fig. 6. Nyquist plots obtained from 30:60:10 electrode before and after 100 CV cycles.

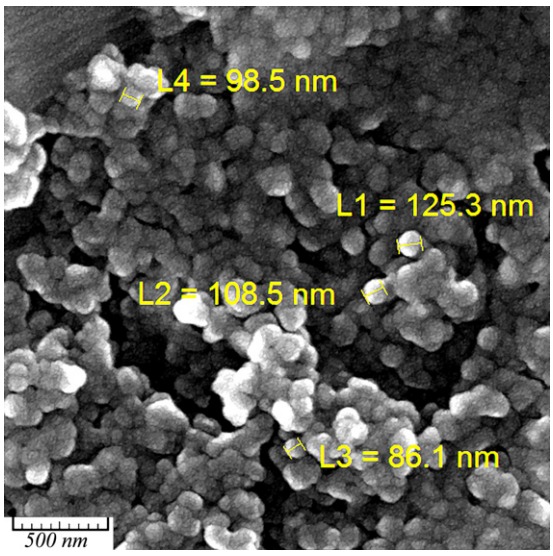

Fig. 7. SEM image obtained from 30:60:10 electrode.

shorter than carbon based materials, because the structure or volume changes during redox reactions leads to the loss of active materials. The stability of 30:60:10 type electrode was evaluated by repeating the CV tests between −0.15 and +0.55 V (vs. SCE) using a scan rate of 10 mV s^{-1}, for 100 cycles (Fig. 5). Simultaneously, EIS method was used to evaluate the electrode changes (Fig. 6). According to Fig. 5, the CV curves show a good reversibility after 100 cycles. According to Fig. 6, Nyquist plots show a double layer capacitance and shift to higher impedances, which confirm the higher equivalent series resistance after 100 cycles. Electrolyte deposition and redox reactions could be the reasons for this resistance increment.

SEM image (Fig. 7) shows the uniform and thin nano particles dispersion on the electrode surface. This increases the specific surface area and makes the electrode porous. This porous surface greatly improves charge storage and charge delivering capability of the electrode.

4. Conclusion

In summary, electrochemical tests revealed that ZrO_2/carbon black nanocomposite, as electrode material for electrochemical capacitors, has good electrochemical performance in the potential range of −0.15 to 0.55 V (vs. SCE) in 2 M KCl electrolyte. It provides a double layer capacitance. 30:60:10 (CB:ZrO_2:PTFE) type electrode has as high as 43.20 F g^{-1} specific capacitance in 2 M KCl electrolyte at scan rate of 10 mV s^{-1} and shows a good cycling performance. 30:60:10 electrode surface shows a porous structure that greatly improves charge storage and charges delivering of electrode capability.

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