

Graphite nanosheets/nanoporous carbon black/cerium oxide nanoparticles as an electrode material for electrochemical capacitors



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ABSTRACT

In this study, effect of morphology and pore size distribution on physicochemical properties of graphite nanosheets (GNSs)/nanoporous carbon black (NCB)/CeO₂ nanoparticle electrodes were investigated in 3 M NaCl electrolyte. 90:00:00:10 (GNS:NCB:CeO₂:PTFE) electrodes show a flat and smooth surface and 75:00:15:10 electrodes showed micro pores which opened on surface. In the presence of NCB particles, electrodes like 25:50:15:10 showed the macro, micro and nano pores, simultaneously. Total charge (q_T) of 1.73, 37.88, 208.33 C g⁻¹ cm⁻² and outer charge to total charge (q_o^*/q_T) of 0.53, 0.43 and 0.24 were obtained from 90:00:00:10, 75:00:15:10 and 25:50:15:10 electrodes, respectively. It is concluded that introducing narrower and deeper pores on surface of electrodes increases the charge storage capability and decreases the current response and power delivering capability. Flat surface of GNSs showed 3.4 F/g and also exhibited good capacitance retention of more than 80%. Additionally, nanoporous structures increased the capacitance of 25:50:15:10 electrodes up to 16.2 F/g at 10 mV s⁻¹ in 3 M NaCl electrolyte.

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1. Introduction

To produce and store energy storage would dramatically increase in future, however the problem of ensuring power quality is our responsibility. Energy storage is being widely regarded as one of the potential solutions to deal with variations of variable renewable electricity sources, and it is the key to unlocking the door of renewable energy. Among different energy storage systems, ultracapacitors are recognized as attractive energy storage devices to satisfy the current and future needs [1]. Electrochemical capacitors have received a great attention in recent years for their high power capability, life cycle (more than 500,000 cycles at 100% depth of discharge) high energy efficiency ranging from 85% up to 98%, and their good reversibility against other power storage devices [2,3].

With respect to electrode materials there are three main categories: carbon base, transition metal oxides and conductive polymers [4]. Almost, common electrodes proposed for

electrochemical double layer capacitors contain carbon base materials, such as activated carbons, carbon black (CB), carbon aerogels, carbon nanotubes (CNTs), graphene, ordered mesoporous carbons and hierarchical porous carbons, that have different specific surface area and pore size distributions [5,6]. Additionally, conductivity, porosity and morphology are shape dependent and the unique characteristics of these materials enhance their electrochemical performance [7–15]. It is reported that porous materials and nanoporous structures show a higher specific surface area. On the other hand, flake and sheet like structures almost show higher accessibility but decreased specific surface area and they may increase the charge transfer rate during charging and discharging processes. On these structures, almost always, less active surfaces and/or internal surfaces are prevented from forming double layer [16,17]. Different morphologies have been reported for carbon base materials; for example, carbon blacks (CBs), CNTs and graphene nanosheets exhibit spherical, tubular and lamellar structures, respectively. On the other hand, oxides and hydroxides of transition metals like Ru [18], Co [19], Zr [20], Mn [21] and Ce [22], and conducting polymers, like polyaniline (PANI) [23] and polypyrrole [24] are of candidate materials for supercapacitors which store energy through pseudo mechanism. These materials possess multiple oxidation states that enable rich redox and Faradic reactions on surface of carbon base materials.

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The aim of this study is to investigate these morphological effects on physicochemical properties of carbon containing nanocomposites as electrode materials for electrochemical capacitors. In this respect, mechanical pressing was used to prepare electrodes. The electrochemical properties of the electrodes were evaluated by cyclic voltammetry, electrochemical impedance spectroscopy and scanning electron microscopy.

2. Experimental

2.1. Material and electrode preparation

High purity (>99%) cerium oxide (CeO_2) (<30 nm) and polytetrafluoroethylene (PTFE) (<2 μm) as a polymeric binder were purchased from Aldrich, USA. Multi-layered graphene nanosheets (GNSs) with a purity of 98.5% purchased from graphene supermarket, USA and nanoporous carbon black (NCB) (<10 nm in pore diameter and <2 μm in particle size) purchased from Degussa, Germany. All the other chemicals used in this study were purchased from Merck, Germany. In order to prepare the electrodes, the mixture containing different wt% of CeO_2 nanoparticles, GNSs, NCB particles and 10 wt% PTFE were well mixed with propeller stirrer at 1200 rpm for 30 min in ethanol bath to form a paste. Prepared mixtures were then sonicated for 90 min. Sonication process was performed at frequency of 20 kHz with an inlet ultrasound power of around 0.5 W mL^{-1} (Hielscher Ultrasound Technology, Germany). Then the prepared pastes were dried, powdered and pressed onto a 316L stainless steel plate ($5 \times 10^7 \text{ Pa}$) which served as a current collector (surface area was 1.22 cm^2). The typical mass of used active material was 30 mg. The used electrolyte was 2 M NaCl.

2.2. Characterization

Electrochemical behavior of prepared electrodes was characterized using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques. The electrochemical measurements were performed using an Autolab (Netherlands) potentiostat Model PGSTAT 302N. CV tests were recorded at scan rates of 10, 20, 30, 50 and 100 mV s^{-1} and 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 prepared electrodes was determined by integrating either the oxidative or reductive parts of cyclic voltammogram curves to obtain the voltammetric charge Q (C). This charge was divided by mass of active material m (g) of electrode and the width of potential window of the cyclic voltammogram ΔE (V), i.e., $C = Q/(m\Delta E)$ [21]. Scanning electron microscopy (TESCAN, USA) was used for better understanding the effect of surface morphology and its nature on physicochemical properties of prepared electrodes.

3. Result and discussion

Fig. 1 shows a schematic of surface morphology of electrodes fabricated. In the absence of NCB and CeO_2 nanoparticles, GNSs deposit on each other and make a flat and smooth surface on the electrode. This type of morphology may act like a barrier against the electrolyte diffusion bath through the electrode material, and may decrease the accessible surface area of the electrode. As shown in Fig. 1, addition of CeO_2 nanoparticles can crack distances between the nanosheets and will make micro pores on the surface of the electrode. These micro pores are almost narrow and deep (about 1 μm in diameter and few μm in depth). On the other hand, transition metal oxides like CeO_2 are non-conductive and electro-active materials that will take part in Faradic reactions. Addition of

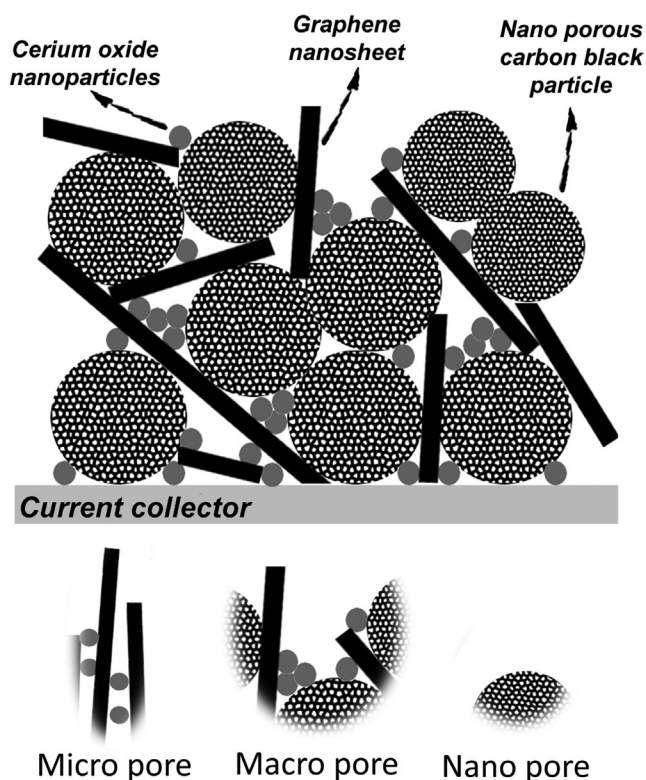


Fig. 1. Schematic illustration of different pores prepared on the electrodes.

nanoporous CB particles (<2 μm in diameter) into the electrode material can act as a mixer due to its large particle size and increases distances between GNSs and re-arranges them in different directions (Fig. 1). These macro pores are almost less than 5 μm in diameter and about 10 μm in depth, which can increase the specific surface area and the ability of electrolyte to diffuse. So, in the presence of GNS, NCB and CeO_2 nanoparticles, surface topography revealed by SEM images suggest that three types of macro, micro and nano pores formed on the surface. As shown in Fig. 1, macro pores are made between the GNSs and NCB particles, micro pores are made between the GNS and CeO_2 nanoparticles and the surface of carbon black containing electrodes is nanoporous. As shown in Fig. 2, SEM images obtained from the surface of 90:00:00:10 (GNS:NCB: CeO_2 :PTFE) electrodes confirm the flat and smooth surface of the electrode (Fig. 2(a)). SEM images obtained from 75:00:15:10 electrodes confirm the presence of micro pores which open on the surface of the electrode (Fig. 2(b)), and NCB and CeO_2 containing electrodes like 25:50:15:10 shows macro, micro and nano pores, simultaneously (Fig. 2(c) and (d)). These will change the specific surface area, electrical resistance, diffusion characteristics and therefore, they can alter the energy storage and rate capacity of the prepared electrodes. Hence, these electrodes were selected for further investigations.

Fig. 3 shows the second CV of prepared electrodes at scan rate of 10 mV s^{-1} in 3 M NaCl electrolyte. CV curves exhibit a rectangular shaped profile which is characteristic of ideal capacitive behavior [25] and show almost potential-independent double layer capacitance over relatively wide range of potential window. Addition of CeO_2 nanoparticles into the electrode (75:00:15:10) increased the charge stored on the electrode slightly (Fig. 3) which may be due to Faradic reactions and increase of specific surface area. The principle reaction involved in charging and discharging processes of cerium dioxide in an aqueous electrolyte can be described by Reaction (1) [?]:

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