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Short Communication

Fabrication of a novel graphene nano-sheet electrode embedded with nano-particles of zirconium dioxide for electrochemical capacitors: Ions-redeposition on the surface of nanoporous electrode

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ABSTRACT

In this paper, the effect of charge/discharge cycles on the electrode containing nano-zirconium oxide, nanoporous carbon black and graphene nanosheets in electrochemical capacitors has been described. Surface morphology and electrochemical performance of the prepared electrode have also been conducted. The electrode prepared from graphene nanosheets (GNS), nanoporous carbon black (NCB), zirconium oxide (ZrO_2), and polytetrafluoroethylene (PTFE) in molar ratio of 54:09:27:10 respectively showed a maximum specific capacitance as high as 11.84 $F\,g^{-1}$ in the potential range between −0.45 and 0.35 V (V vs. SCE) at a scan rate of 10 $mV\,s^{-1}$ in a 3 M NaCl electrolyte. The electrochemical results show the low ratio of the outer to total charge (q_O^*/q_T^*) which confirms the low current response and higher voltage reversal at the end potentials. SEM images confirms the ions re-deposit as agglomerates and accompanied by a drastic decrease in the surface area on the surface of the electrode after one charge/discharge cycle.

1. Introduction

Electrochemical capacitors also known as supercapacitors in recent terminology although known since 1957 [1–3] have undergone a dramatic transformation in recent years because of their promising potential to deliver more power than batteries and store more energy than conventional capacitors. An understanding of the greater charge mechanism role of nano-materials, dissolution kinetics of solvated ions in the pores has led to the higher capacitance of electrochemical capacitors by using carbon electrodes and opened the door for high energy devices. Nanomaterials provide high electrical conductivity, short ion diffusion pathways, and can provide an excellent interfacial integrity to the system. Currently, many laboratories are actively engaged in the development of new types of electrode materials, and most of the research has been focused on the development of nanoporous materials for electrochemical capacitors [4,5]. Although the demand for developing new porous electrode materials with higher specific surface area is increasing, the problem of electrolyte ions re-deposition on the pore walls and blocking

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them is very challenging. Re-deposition of electrolyte ions and active materials on the electrode decreases the active specific surface area and the charge stored on the electrode. Transition metal oxides are considered to be the most suitable candidate materials for electrochemical capacitors. 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. As investigated by Nasibi et al. zirconium oxide demonstrate capacitive behavior in 2 M KCl electrolyte [6].

The aim of this paper is to investigate the charge distribution ability of nanoporous NCB/GNS/ZrO_2 electrode and the effect of electrolyte ions and active material re-deposition on this electrode. Mechanical pressing was used as a fast and easy method to fabricate the electrode. The products were then evaluated as possible candidate electrode materials for electrochemical capacitors using techniques including cyclic voltammetry, electrochemical impedance spectroscopy and scanning electron microscopy.

2. Experimental

2.1. Materials

Nanoporous (<10 nm in diameter) carbon black (NCB) micro-sized particles ($<2\,\mu m$) were purchased from Degussa, Germany. Graphene nanosheets (GNS) (60 nm Flakes, multi-layered) with the specific surface area of 15 m^2/g and a purity of 98.5% were purchased from Graphene Supermarket, USA. Polytetrafluoroethylene (PTFE) micro-sized powder ($<2\,\mu m$) and high-purity ($>99\%$) nano-sized zirconium oxide (ZrO_2) particles (<100 nm) were purchased from Aldrich, Germany. All of the other chemicals used were purchased from Germany (to purchase these materials, visit the websites www.graphenesupermarket.com, http://www.sigmaaldrich.com and www.merckgroup.com(. In order to prepare the electrode, a mixture containing 54 wt% of GNS, 9 wt% NCB, 27 wt% ZrO_2 nanoparticles and 10 wt% PTFE was mixed well in ethanol to form a paste and then was pressed (at 50 MPa pressure) onto the 316 L stainless steel substrate, which served as a current collector (having a surface area of 1.4 cm^2). The typical mass of electrode material was 45 mg. The electrolyte used was 3 M NaCl.

2.2. Characterization

The electrochemical behavior of the prepared electrode was characterized using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests. The electrochemical measurements were conducted using an Autolab (Netherlands) potentiostat Model PGSTAT 302N. CV tests were carried out within the range of -0.45 to

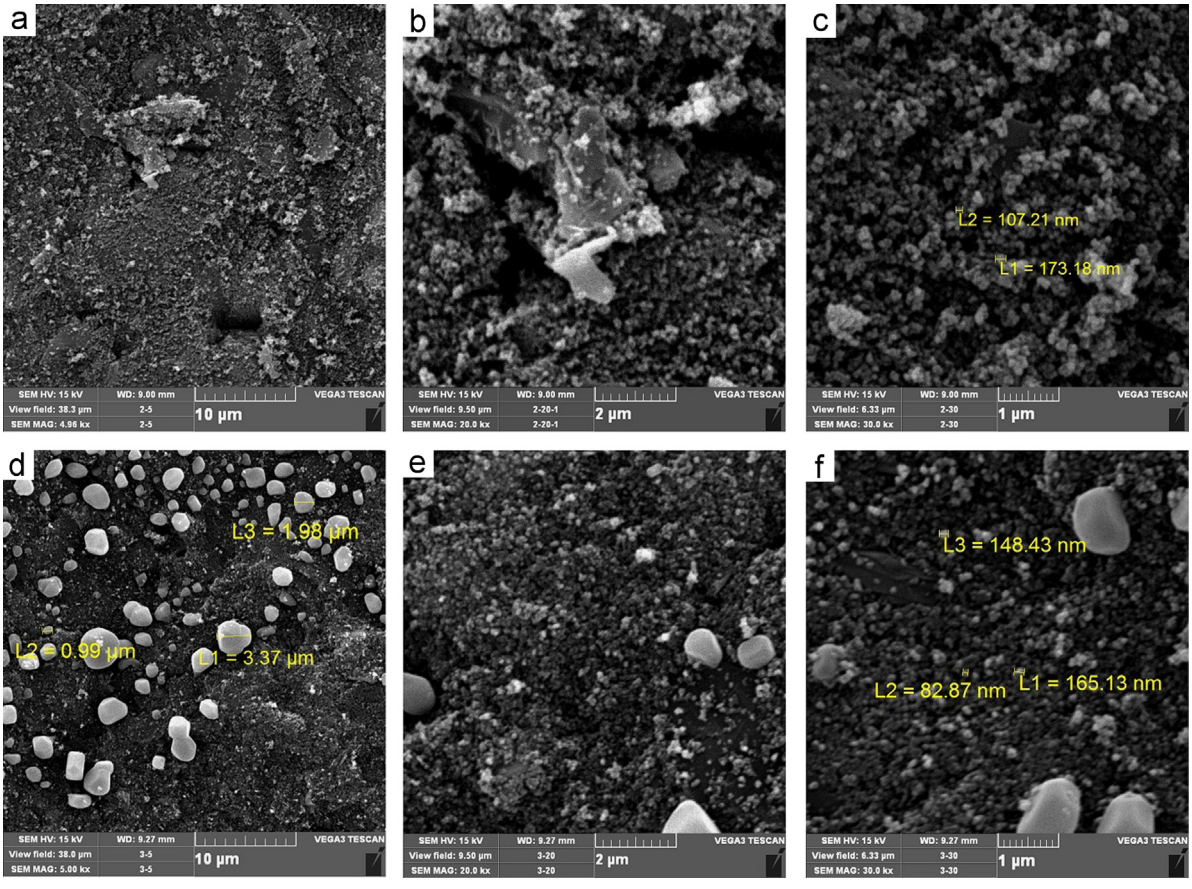

Fig. 1. SEM images obtained from 54:09:27:10 electrode before (up) and after (down) charging/discharging cycles.