Materials Research Bulletin 60 (2014) 5–9

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Electrochemical performance studies of MnO_2 nanoflowers recovered from spent battery

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ARTICLE INFO

Article history:
Received 11 February 2014
Received in revised form 1 August 2014
Accepted 11 August 2014
Available online 13 August 2014

Keywords:
Electrochemical properties
Energy storage
Nanostructures
Oxides

ABSTRACT

The electrochemical performance of MnO_2 nanoflowers recovered from spent household zinc–carbon battery is studied by cyclic voltammetry, galvanostatic charge/discharge cycling and electrochemical impedance spectroscopy. MnO_2 nanoflowers are recovered from spent zinc–carbon battery by combination of solution leaching and electrowinning techniques. In an effort to utilize recovered MnO_2 nanoflowers as energy storage supercapacitor, it is crucial to understand their structure and electrochemical performance. X-ray diffraction analysis confirms the recovery of MnO_2 in birnessite phase, while electron microscopy analysis shows the MnO_2 is recovered as 3D nanostructure with nanoflower morphology. The recovered MnO_2 nanoflowers exhibit high specific capacitance (294 $F\,g^{-1}$ at 10 $mV\,s^{-1}$; 208.5 $F\,g^{-1}$ at 0.1 $A\,g^{-1}$) in 1 M Na_2SO_4 electrolyte, with stable electrochemical cycling. Electrochemical data analysis reveal the great potential of MnO_2 nanoflowers recovered from spent zinc–carbon battery in the development of high performance energy storage supercapacitor system.

1. Introduction

Zinc–carbon battery is frequently used in electronic and electrical appliances as it is the least expensive battery among primary batteries. Fresh zinc–carbon battery consists of Zn metal as anode and MnO_2 powder as cathode. In discharged form, Zn is present as ZnO, while Mn is present as Mn_2O_3 and Mn_3O_4 [1–3]. Research shows that Zn and Mn contents are 28.3% and 26.3%, respectively of the total mass in a spent zinc–carbon battery [2]. Such high Zn and Mn contents highlight the importance of battery recycling, both from economy and environment perspectives. Battery recycling can be divided into pyrometallurgical process and hydrometallurgical process. The former involves selective volatization of scrapped battery at elevated temperature followed by condensation for metal recovery. It is the most popular battery recycling process in industry due to its simplicity as battery dismantling is not required [3–6]. On the other hand, hydrometallurgical process involves dismantling, pre-treatment followed by metal ions leaching and precipitation. Hydrometallurgical process is more efficient in metal recovery and environmental friendly as its energy consumption is lower [7,8]. A comparison of these processes is reported elsewhere [9], with detail technical information about battery treatment. However, battery recycling activities are not favored all the time as the economic interests normally supersede the environmental obligations. Therefore, recycling spent battery into valuable product is expected to be a solution in this context. In this work, we study the feasibility of recovered MnO_2 from spent zinc–carbon battery in supercapacitor application.

Supercapacitor is an energy storage device that stores energy via ion adsorption (electrochemical double layer capacitor) or fast surface redox reaction (pseudocapacitor). It has attracted worldwide research interests, mainly attributed to its high power capability, fast charging time, excellent reversibility and long cycle life [10]. In terms of energy and power aspects, supercapacitor positions between battery and conventional capacitor where it is preferred when high power load is needed. Recent years, various materials have been developed for supercapacitor electrode and they can be categorized into carbon-based materials (activated carbon, carbon nanotubes, graphene, fullerene) [11–14], transition metal oxides ($RuO_2{\cdot}H_2O$, MnO_2, Co_3O_4, V_2O_5) [15–18], and conductive polymers (polyaniline, polypyrrole) [19,20]. Among these materials, transition metal oxides show superiority over the rest due to their high specific capacitance. $RuO_2{\cdot}H_2O$ is a remarkable transition metal oxide as it can contribute specific capacitance up to 1585 $F\,g^{-1}$ [15]. Nonetheless, its commercial

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http://dx.doi.org/10.1016/j.materresbull.2014.08.008
0025-5408/