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Solid state synthesis of $Li_{0.33}MnO_2$ as positive electrode material for highly stable 2V aqueous hybrid supercapacitors:

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ABSTRACT

In this paper we present a comprehensive structural, chemical and electrochemical characterization of monoclinic $Li_{0.33}MnO_2$ as a positive electrode material for aqueous high-voltage hybrid supercapacitors. The monoclinic $Li_{0.33}MnO_2$, which is traditionally used as cathode material for lithium ion batteries, was synthesized through a simple thermal solid-state synthesis. The monoclinic $Li_{0.33}MnO_2$ electrode exhibits a wide operational potential window ranging between −1.25 and 1.25 V vs SCE, which enables it to serve as either a negative or a positive electrode. In addition, this electrode material exhibits a high specific capacity of 140 mAh g^{-1} at a low current density of 0.1 A g^{-1}, and 76 mAh g^{-1} at high current density of 1 A g^{-1} in this range of potentials. Hybrid supercapacitors composed of $Li_{0.33}MnO_2$ positive electrode and activated carbon (AC) negative electrode were fabricated. They exhibit outstanding electrochemical performance in terms of operational potential window, cycleability, and energy and power density. The $Li_{0.33}MnO_2$/AC hybrid capacitor has an energy density of 13.5 Wh kg^{-1} at power density of 100 W kg^{-1}, which is twice than that of MnO_2/AC and AC/AC supercapacitors, and an energy density of 7 Wh kg^{-1} at 1000 W kg^{-1}, which is seven times higher than that of AC/AC capacitors at this power density. Furthermore, this hybrid capacitor presents an excellent cycle life with 80% specific capacitance retention after 12,000 cycles to 2 V. The electrochemical charge storage mechanism of the monoclinic $Li_{0.33}MnO_2$ was investigated by cyclic voltammetry and X-ray diffraction.

1. Introduction

In recent years, electrochemical energy storage and conversion devices have been the subject of intensive investigation, due to increasing awareness of global warming, the limited resources of fossil fuels, and the growing need for reduced emissions and green energy sources. Supercapacitors have attracted the attention of many research groups owing to their ability to provide higher power density and much longer cycle life than batteries [1–3]. However, supercapacitors suffer from low energy density compared to batteries due to their distinctive electrochemical processes, which give rise to different charge storage mechanisms.

The main challenge in the supercapacitors field is to increase the energy density without sacrificing the high power density characteristics, while using low cost environmentally friendly materials. The energy density of supercapacitors is proportional to the voltage established between the electrodes (ΔV) and the specific capacitance (C) according to the following equation:

$$E = \frac{1}{2} C \, \Delta V^2 \tag{1}$$

The parameters which determine the electrical energy stored in a supercapacitor are determined by its components, namely the electrolyte solution and the electrode materials. The maximal voltage which can be established between the electrodes of the supercapacitor is usually determined by the electrochemical stability of the electrolyte solution [4] and the catalytic activity of the electrode materials. There are three main types of electrolyte solutions: aqueous, organic, and ionic liquids. Among these electrolyte solutions, aqueous electrolyte solutions present the

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highest ionic conductivity and are considered the most safe and environmentally friendly. These features, in addition to relatively low cost and less rigorous packing requirements, make aqueous electrolyte solutions more desirable from an industrial point of view. However, the main drawback of aqueous solutions is the relatively narrow potential window of water compared to organic or ionic liquid electrolyte solutions. One of the keys to overcome this drawback is to fabricate asymmetric supercapacitors, which are composed of two electrode materials with well-separated potential windows and high overpotential for hydrogen and oxygen evolution [5–7].

The specific capacitance of the system depends mainly on the electrode materials, its charge storage mechanism, and its accessible surface area for the electrolyte ions [4]. Among the electrode materials, large surface-activated carbons (AC) and pseudocapacitive metal oxides (MO) are the most studied. The main AC charge storage mechanism is electrostatic interaction. The potential applied to AC electrodes does not promote faradaic reactions, but rather adsorption of electrolyte ions on the surface, which is compensated by electron transfer to the external circuit. On the one hand, carbonaceous electrode materials enable working at high power densities, but on the other hand the capacitive process of AC electrodes is limited to the accessible surface area of the electrode, resulting in limited specific capacitance. As opposed to the capacitive charge storage mechanism in carbonaceous materials, pseudocapacitive metal oxides such as RuO_2, MnO_2 and Fe_3O_4 involve surface faradaic reactions, resulting in relatively high specific capacitance, i.e. energy density [8]. Many studies demonstrate the great potential of MOs, especially MnO_2, as electrode material for supercapacitors [7,9–15]. However, monoclinic Li_XMnO_2, which has been traditionally used as cathode material for Li ion batteries [16–22], was barely studied as an electrode material in the field of supercapacitors, despite its improved stable structure and conductivity relative to pure MnO_2 [23].

In this study we synthesized $Li_{0.33}MnO_2$ by a simple solid-state synthesis using low-cost chemically-prepared manganese dioxide (CMD) and lithium nitrate. Practically thick electrodes were tested in this work. The electrochemical performance of the AC and $Li_{0.33}MnO_2$ electrodes was characterized in 2 M Li_2SO_4 aqueous solutions using three-electrodes cells, followed by optimization and fabrication of mass-balanced asymmetric two electrodes cells. The structural and physical characteristics of the synthesized product were investigated in detail using microscopic and spectroscopic techniques.

2. Experimental

2.1. Materials

CMD and $LiNO_3$ precursors were obtained from Erachem Inc. and Alfa-Aesar, respectively. Activated carbon powder was received from EnerG2 (USA), and Li_2SO_4 was purchased from Sigma-Aldrich. The carbon additive for enhancing electrode conductivity – Super P carbon black, was purchased from Timcal (Switzerland), and non-woven cellulose separators were obtained from NKK (Japan). The electrolyte aqueous solution was prepared using doubly-distilled water.

2.2. Synthesis of $Li_{0.33}MnO_2$

$Li_{0.33}MnO_2$ was synthesized by mixing chemically-prepared manganese dioxide (γ-MnO_2 phase) and $LiNO_3$ at a 3:1 molar ratio, followed by heat treatment at 370 C° under nitrogen atmosphere and atmospheric pressure for 20 hours, as demonstrated by Aurbach et al. [17].

2.3. Materials chemical and physical characterizations

Nitrogen impurities from the synthesis process were determined using CHNS-O elemental analysis (EA1110 model from the Thermo Company). Manganese and lithium elemental analysis was performed using atomic absorption spectroscopy (PerkinElmer atomic absorption spectrometer, AAnalyst400 system). The CMD and the lithiated product crystallinity were investigated by X-ray diffraction (XRD) using an AXS D8 Advance diffractometer (θ–θ reflection geometry, Cu Kα radiation, receiving slit 0.2 mm, scintillation counter, 40 mA, 40 kV) from Bruker, Inc. The morphology and additional study of the crystallinity were conducted using transmission electron microscopy (TEM) and high-resolution TEM (JEOL 2100 LaB6 model, operating at 200 kV).

2.4. Electrodes preparation

The activated carbon (AC) and $Li_{0.33}MnO_2$ electrodes were prepared by mixing the active material, carbon black, poly (tetrafluoroethylene) (PTFE) and isopropanol (2-propanol or isopropyl alcohol) at weight ratios of 70:20:10 for the $Li_{0.33}MnO_2$ electrodes and 85:5:10 for the AC electrodes. The obtained doughy mixtures were then pressed into 150-μm thick stand-alone films and then were dried under vacuum. These thick electrodes could be measured without the use of special current collectors. They were attached to glassy carbon pistons in T type cells. These glassy carbon pistons served as effective current collectors and electrical contacts for the electrodes.

2.5. Electrochemical measurements

The electrochemical tests were performed with computerized potentiostat/galvanostat instruments from Bio-Logic Inc. First, each electrode was electrochemically characterized. For this purpose we used three-electrodes T-cells composed of AC counter electrodes, which were twice in size than the working electrode, and saturated calomel (SCE) as a reference electrode. Electrochemical characterization of the full supercapacitors was conducted using T-cells after electrodes mass balancing. In this study all the electrochemical measurements were performed with 2 M Li_2SO_4 aqueous electrolyte solutions.

The charge-storage mechanism and electrochemical stability windows of each electrode and of the full cells were evaluated by cyclic voltammetry. The specific capacitance C_s, coulombic efficiency, average energy $E_{average}$, and average power density $P_{average}$ were calculated by galvanostatic charge–discharge measurements using the following equations:

$$C_S = \frac{i\Delta t}{\Delta V m}\ (\mathrm{F\ g^{-1}}), \tag{2}$$

$$P_{average} = \frac{\Delta V i}{2m} 1000\ (\mathrm{W\ kg^{-1}}), \tag{3}$$

$$E_{average} = \frac{P_{real}\Delta t}{3600}\ (\mathrm{Wh\ kg^{-1}}), \tag{4}$$

$$\text{coulombic efficiency} = \frac{\Delta t_{discharge}}{\Delta t_{charge}} \times 100 \tag{5}$$

where i (A) is the input constant current, Δt (sec) is the discharge time (unless stated otherwise), ΔV (V) is the potential difference between the end of the charge and the end of the discharge, and m