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Short communication

Characterization of $MnFe_2O_4/LiMn_2O_4$ aqueous asymmetric supercapacitor

Yen-Po Lin, Nae-Lih Wu*

Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan

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ABSTRACT

A new type of asymmetric supercapacitor containing a $MnFe_2O_4$ negative electrode and a $LiMn_2O_4$ positive electrode in aqueous $LiNO_3$ electrolyte has been synthesized and characterized. The nanocrystalline $MnFe_2O_4$ anode material has a specific capacitance of 99 F g^{-1} and the $LiMn_2O_4$ cathode a specific capacity of 130–100 mAh g^{-1} under 10–100 C rate. The cell has a maximum operating voltage window of ca. 1.3 V, limited by irreversible reaction of $MnFe_2O_4$ toward reducing potential. The specific power and specific energy of the full-cell increase with increasing anode-to-cathode mass ratio (A/C) and saturate at A/C ~4.0, which gives specific cell energies, based on total mass of the two electrodes, of 10 and 5.5 Wh kg^{-1} at 0.3 and 1.8 kW kg^{-1}, respectively. The cell shows good cycling stability and exhibits significantly slower self-discharge rate than either the $MnFe_2O_4$ symmetric cell or the other asymmetric cells having the same cathode but different anode materials, including activated carbon fiber and MnO_2.

1. Introduction

Asymmetric supercapacitors are promising energy storage devices, being capable of charging/discharging faster than batteries and having higher energy densities than traditional electric double-layer capacitors (EDLCs). Based on the electrochemical properties of the electrode materials, they can in general be divided into two major categories. The first kind of asymmetric supercapacitors contains two electrodes of different materials exhibiting capacitive behavior over different potential ranges so that the overall operation voltage window of the cell can be enlarged and its energy density becomes greater than the symmetric cells containing solely either kind of the electrodes [1–3]. The second type combines a battery electrode with a capacitor electrode in one cell [4–6]. As the battery electrode charges/discharges at a plateau potential, the cell is capable of storing a greater amount of energy than the symmetric cell of the capacitive electrodes even within the same operating voltage window. Most of the existing examples of this category [5,6], such as activated carbon (AC)/PbO_2 and AC/NiO, employ an EDLC material for the capacitor electrode. The only cell, to our knowledge, that uses pseudocapacitve material for this purpose is $MnO_2/LiMn_2O_4$ [7] with a Li^+-containing organic electrolyte. However, the cell was not tested for cycle-life and self-discharge characteristics.

Nanocrystalline $MnFe_2O_4$ is a pseudocapacitive material possesses high-power delivering capability [8–10]. In contrast to MnO_2-based pseudocapacitive materials, which are essentially amorphous, $MnFe_2O_4$ exhibits pseudocapacitance in crystalline form, and its symmetric cell has been shown to exhibit superior cycling stability than the amorphous-MnO_2 ones in aqueous electrolytes [9]. In this work, a new type of asymmetric supercapacitor which consists of a $MnFe_2O_4$-carbon black composite, abbreviated as $MnFe_2O_4$@C, anode and a $LiMn_2O_4$ cathode has been synthesized and characterized for its fundamental operating characteristics, including energy and power capabilities, cycling stability and self-discharge behavior.

2. Experimental

The preparation procedure for the $MnFe_2O_4$@C composite powder, which has an oxide-to-carbon mass ratio of 74:26, has been described in detail elsewhere [8,9]. In brief, aqueous solution containing $MnSO_4$ and $FeCl_3$ (Mn^{2+}:Fe^{3+} = 1:2) and predetermined amount of carbon black powder was simultaneously introduced into a 1.5 M $NaOH_{(aq)}$ solution under vigorous stirring. Black precipitate formed immediately upon mixing, and was subsequently washed with de-ionized water to remove residual anions. Finally, the powder was dried in air at 50 °C, followed by calcination at 350 °C in N_2 for 2 h. $LiMn_2O_4$ was a courtesy from Industrial Technology Research Institute, Taiwan.

The cathode electrode contained 63 wt% $LiMn_2O_4$, 25 wt% KS6 (Timcal), 5 wt% Super P (Timcal) and 7 wt% polyvinylidene fluoride (PVdF, Aldrich), while the anode contained 93 wt% $MnFe_2O_4$@C and 7 wt% PVdF. Both electrodes used Ti foil as current collector, and the active-layers were prepared by a slurry-casting method using N-methylpyrrolidone (NMP; Mitsubishi Chemical) as solvent. The electrodes were finally dried at 120 °C in an oven for 6 h.

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* Corresponding author. Tel.: +886 2 23627158; fax: +886 2 23623040.
E-mail address: nlw001@ntu.edu.tw (N.-L. Wu).

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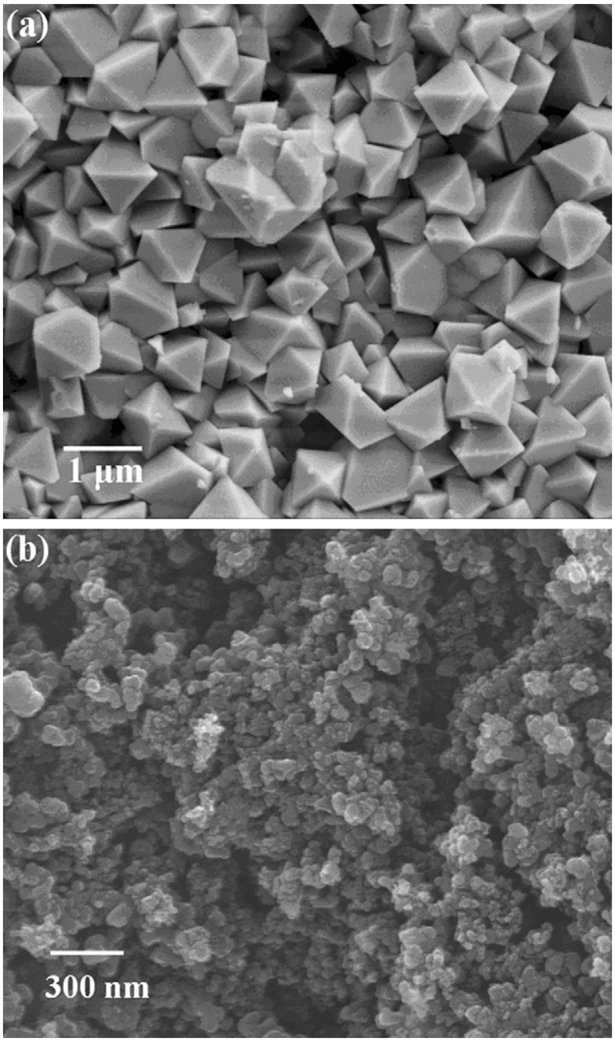

Fig. 1. SEM micrographs of (a) $LiMn_2O_4$ and (b) $MnFe_2O_4$@C composite.

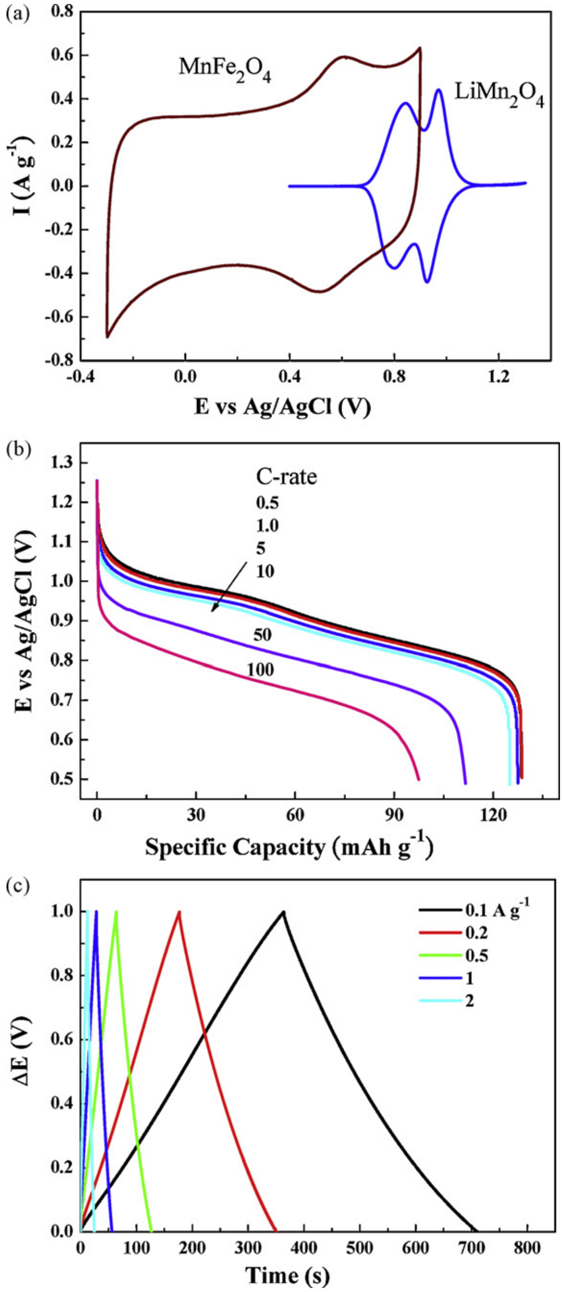

Fig. 2. Electrochemical characterization of individual electrodes: (a) voltammograms of $MnFe_2O_4$@C anode (4 mV s^{-1}) and $LiMn_2O_4$ cathode (0.2 mV s^{-1}); (b) galvanostatic discharge potential curves of $LiMn_2O_4$ cathode; (c) galvanostatic charge/discharge voltage curves of the $MnFe_2O_4$ symmetric cell (the current densities are based on the mass of $MnFe_2O_4$@C in one electrode.).

Full-cells were assembled with the two electrodes face-to-face and a porous separator (BS0712, Coin Nano Tech) in between. The measurements were typically carried out with the cells immersed in excess amount of electrolyte, except for the cycling-stability studies, where the cells were removed from the electrolyte container and tested in an empty sealed container. All electrochemical analyses were conducted on an electrochemical analyzer (CHI 405a, CH Instrument). The three-electrode configuration, which consisted of a Pt counter electrode, a Ag/AgCl/saturated $KCl_{(aq)}$ (EG&G, potential is 197 mV versus NHE at 25 °C) reference electrode and a working electrode, was employed to characterize the electrochemical behaviors of individual electrodes. The potentials mentioned hereafter are based on this reference electrode. The two-electrode configuration, however, was adopted for the full-cell characterization. In some full-cell experiments, the potential of each of the electrodes were independently monitored against a reference electrode.

3. Results and discussion

3.1. Individual materials and electrodes

The spinel $LiMn_2O_4$ crystallites have an octahedral shape with a rather uniform particle size close to 1.0 μm (Fig. 1a). In contrast, the $MnFe_2O_4$@C powder contains rounded particles with sizes no greater than a few tens nanometers (Fig. 1b). The average crystal size of $MnFe_2O_4$, as determined from the line-broadening of X-ray diffraction peak, is 13 nm, while the N_2-adsorption BET surface area is 160 m^2 g^{-1}.

Fig. 2a compares the voltammograms of the individual electrodes. $MnFe_2O_4$@C anode showed reversible capacitive behavior within −0.3 and 0.9 V. Irreversible reduction of the oxide electrode becomes significant below −0.3 V, while irreversible oxidation starts to occur above 0.9 V. A pair of redox humps centered at ~0.6 V results mainly from charge transfer at the Fe-ion sites [10], while the charge transfer at the Mn-ion sites occurs throughout the entire potential range. The capacitance of the $MnFe_2O_4$@C composite is 69 F g^{-1} at 4 mV s^{-1}. As the specific capacitance of the carbon