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1.2 Volt manganese oxide symmetric supercapacitor

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ABSTRACT

Capacitance fading of MnO_2 supercapacitor electrode under negative polarization below 0.0 V (versus Ag/AgCl/sat. $KCl_{(aq)}$) arises from extensive reduction of Mn(IV) to form inactive Mn(II) species, and this has typically limited the operating voltage window of an aqueous symmetric MnO_2 supercapacitor to be no greater than 0.8 V. As this lower potential limit is close to the onset potential of MnO_2-catalyzed oxygen reduction reaction (ORR), the fading problem can be alleviated by effectively passing the accumulated electrons in the oxide electrode to the dissolved oxygen molecules in electrolyte in order to avoid the formation of the surface Mn(II) species. This has been demonstrated by either increasing the dissolved oxygen content or using the Ti(IV)/Ti(III) redox couple in the electrolyte as a charge-transfer mediator to enhance the electrocatalytic activity of MnO_2 for ORR. Therefore, a MnO_2 symmetric supercapacitor showing remarkable cycling stability over an operating voltage window of 1.2 V has been achieved by using Ti(IV)-containing neutral electrolyte (1 M $KCl_{(aq)}$).

1. Introduction

MnO_2 has been intensively studied as a supercapacitor electrode material in neutral aqueous electrolytes. It possesses the advantages of low cost, sufficiently high specific capacitance, and environmentally friendly nature [1]. The operating voltage window is a critical parameter, considering the voltage square dependence of energy and power densities, of a capacitor cell. Unfortunately, the voltage window of the aqueous symmetric MnO_2 supercapacitor has typically been limited to be less than 1.0 V [2]. For example, in the case of $KCl_{(aq)}$ electrolyte, it has been shown that MnO_2 electrode suffers from obvious capacitance fading either below 0.0 V (versus Ag/AgCl/sat. $KCl_{(aq)}$) under negative polarization, due to formation of inactive Mn(II) surface species, or above 1.0 V under positive polarization, owing to extensive oxygen oxidation along with electrode passivation [3,4]. Amorphous MnO_2 electrode has a typical open-circuit potential (OCP) of 0.4 V in a neutral aqueous electrolyte, and therefore the overall workable voltage window of a symmetric MnO_2 supercapacitor is limited to 0.8 V. Komaba et al. [5] once reported the success of suppressing capacitance fading down to −0.1 V by introducing small amount of either $NaHPO_4$ or $NaHCO_3$ into electrolyte. This might allow for a voltage window of 1 V for the symmetric MnO_2 cell, although such a cell was not demonstrated.

The present work provides new insight into the capacitance fading issue of MnO_2 electrode under negative polarization and suggests a new approach to achieve symmetric MnO_2 supercapacitor cell with significantly widened, 1.2 V, operating voltage window.

2. Experimental

MnO_2 particles were synthesized by redox reaction between $KMnO_4$ and $MnSO_4$ aqueous solutions with a Mn(VII)/Mn(II) molar ratio of 2:3 at 25 °C. After being thoroughly washed with de-ionized water, the particles were finally heated at 200 °C for 1 h in air. To prepare the electrode, slurry containing the oxide powder, acetylene black (AB) and polyvinylidene difluoride (PVdF) dispersed in N-methyl pyrrolidone (NMP), was coated onto Ti foils, and finally dried at 120 °C for 6 h in vacuum. On the dry basis, the oxide to AB ratio was at 7:3, while the binder had a weight composition of 14%. Cyclic voltammetry (CV) was carried out on an electrochemical analyzer (Eco Chemie PGSTAT30). A beaker-type electrochemical cell which consists of a Pt counter electrode, a reference (Ag/AgCl/saturated $KCl_{(aq)}$; EG&G; 197 mV versus NHE at 25 °C), and a square shaped MnO_2 electrode with surface area of 1×1 cm^2 as working electrode was employed to characterize the electrochemical behaviors of single MnO_2 electrode, i.e., the so-called "half-cell". Symmetric full-cells were assembled with two square shaped MnO_2 electrodes with surface area of 2.5×2.5 cm^2 arranged face-to-face and a porous separator (BS0712, Coin Nano Tech) in between. The cell was first immersed in excess amount of electrolyte for 24 h and then removed from the electrolyte container and tested in an empty sealed container. This is intended to simulate the situation typically encountered in a practical cell, where the amount of electrolyte is limited. The electrolyte was aqueous 1 M KCl with pH = 7, while the potential scan rate was fixed at 50 mV s^{-1}. Voltage scan has been started and

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ended at the lower-end of the voltage window. The capacitance of the electrode was determined from the voltammograms according to the following equation:

$$C_{avg} = \Delta V^{-1} \int Is^{-1} dV$$

where C_{avg} is the average specific capacitance, ΔV is the scanned potential or voltage window, I is current, and s is voltage scan rate.

Subsequent to cycling, the electrodes were washed with deionized water and dried at room temperature prior to x-ray photoelectron spectroscopy (XPS) analyses. XPS analysis employed an Al K X-ray source operated at 15 kV and 100 W, and used a beam size of 400 μm and pass energy of 20 eV for spectrum acquisition. Sputtering gun was operated at 3 kV and 1 μA with a sputtering area of 2×2 mm^2 and sputtering time of 2 min.

3. Result and discussion

The fresh MnO_2 particles are agglomerates of nanoflakes with the widths in the range of 10–30 nm [3]. The cycling stability of single MnO_2 electrode within the potential window of −0.2 to 0.4 V was tested by using CV scanning, and the variations of specific capacitance under different conditions are summarized in Fig. 1a. First, in order to investigate the effect of oxygen dissolved in electrolyte, the electrolyte was purged with either argon or air for at least 1 h prior to measurements. Hereafter, the electrodes cycled in Ar-purged electrolyte, air-purged electrolyte and blank electrolyte (electrolyte without any prior gas-purging treatment) are denoted as S–Ar, S–O_2 and S–B, respectively. The S–B electrode has an initial specific capacitance 65 Fg^{-1} at 50 mV s^{-1} based on the mass of entire active-layer. As shown in Fig. 1a, the capacitance of the S–B electrode initially decreases monotonously within the first 1000 cycles and then levels off at ca. 50% of the initial value. The capacitance of the S–Ar electrode, which has an initial specific capacitance of 58 Fg^{-1}, exhibits very similar fading pattern. They are consistent with our previous findings [3]. In great contrast, the S–O_2 electrode, which has a slightly higher specific capacitance (77 Fg^{-1}), shows no fading up to 3000 cycles. Fig. 1b illustrates the voltammograms of selected cycles of the S–B electrode. One clearly sees a prominent reduction tail below 0.0 V for the initial cycles, while there is no additional oxidation counterpart occurring during the anodic scan. Upon continuous cycling, while the capacitance decreases, the intensity of the low-potential reduction tail also diminishes. The reduction tail is no longer recognizable when the capacitance fades to the plateau value after ca. 1000 cycles. Before the capacitance of the electrode reaches the plateau, the total amount of charge passed during each cathodic scan is always higher than that of the corresponding anodic scan, suggesting irreversible electrode reduction. As shown in our previous study [3], the average Mn valence on the electrode surface has been reduced to +2.0 after cycling.

The data of the S–O_2 electrode (Fig. 1a and c), on the other hand, clearly indicates that the capacitance fading problem is alleviated by increasing the oxygen content in the electrolyte. These results suggest that the dissolved oxygen be involved in maintaining the electrode activity. One notes that MnO_2 materials have also been studied as alternative cathodic catalysts to platinum (Pt) in air-cathode microbial fuel cells (MFCs) for oxygen reduction reaction (ORR) [6,7]. In such a process, the reduced Mn(III) species transfer electron to the O_2 molecule and itself is oxidized back to Mn(IV), i.e.,

$$2Mn(III) + 1/2O_2 + H_2O \leftrightarrow 2Mn(IV) + 2OH^- \quad (1)$$

This process is facilitated by the fact that the Mn(III)/Mn(IV) redox potential is close to the onset potential of the ORR [8]. It is inferred that the same ORR helps to pass electrons to the dissolved oxygen in the electrolyte when MnO_2 is negatively charged to below 0.0 V in the O_2-saturated electrolyte in the S–O_2 cell so that the formation

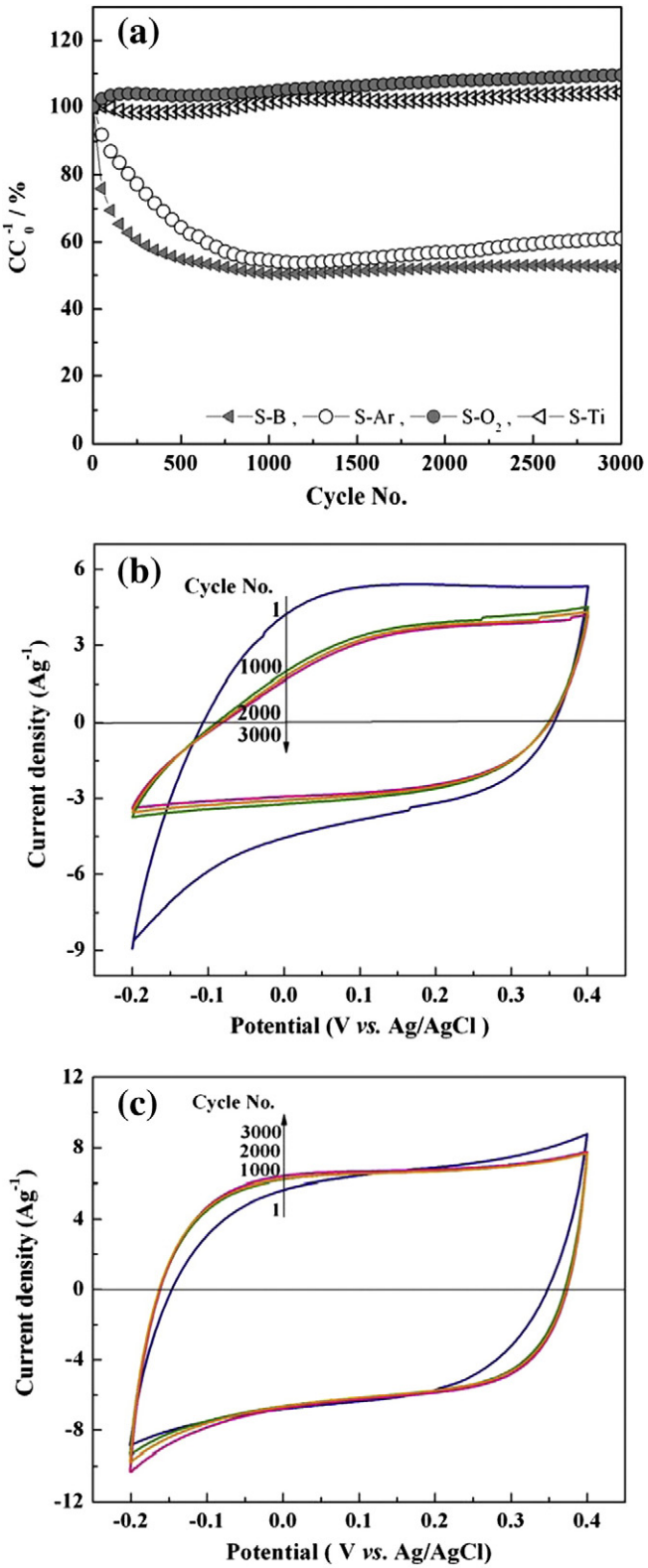

Fig. 1. (a) Capacitance retention (CC_o^{-1}), normalized based on the capacitance of the second cycle (C_o), versus cycle number for the MnO_2 half-cells containing electrolyte without additive under ambient atmosphere (S–B), Ar-purged electrolyte (S–Ar), air-purged electrolyte (S–O2) and electrolyte with Ti(IV) ions as additive (S–Ti) and cycled within the potential window of −0.2 to 0.4 V versus Ag/AgCl/sat. $KCl_{(aq)}$ reference electrode; (b) cyclic voltammograms of selected cycles for the S–B cell electrode; (c) cyclic voltammograms for the S–Ti cell (scan rate = 50 mV s^{-1}; 1 M KCl(aq)).