Organic Electrochemical Capacitor of $MnFe_2O_4$ with Li-Ion Electrolyte

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$MnFe_2O_4$ nanocrystallites have been found to exhibit capacitive characteristics in organic electrolyte containing 1M $LiPF_6$ in mixture of ethyl carbonate + ethylene methyl carbonate up to 4.5 V versus Li/Li^+. The ferrite exhibits a capacitance of 126 F/g-$MnFe_2O_4$, and the symmetric-cell demonstrated a workable voltage window of 2.5 V. *In-situ* synchrotron spectroscopic analysis identified valence change at Mn-ion sites and very small (<1%) extent of lattice variation, in response to Li-ion insertion/extraction. Compared with other pseudocapacitive oxides with Li-ion electrolytes, the present ferrite system has demonstrated superior cycling stability under high-rate cycling.

Synchrotron X-ray absorption near-edge spectroscopy (XANES) was conducted respectively at beam line 17C1 of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan, R.O.C. *In-situ* XANES spectra of Mn K-edge and Fe K-edge of the composite powder were shown in Fig. 1a and Fig. 1b respectively. In Fig. 1a XANES spectrum can be divided into a pre-edge region A (~ 6537-6545 eV) containing weak peaks, a main edge region B (6545-6555 eV), and resonance peak regions C (6555-6566 eV) and D (6566-6580 eV). The peaks within pre-edge region A are ascribed to 1s → 3d transitions. The main absorption region B can be assigned to the transition from 1*s* to *p*-like states of t_{1u} symmetry. The edge energy is conventionally taken as the energy at the first inflection point, and it is known to increase with increasing valence of the transition metal ion within the oxides. It has previously been found that the Mn ions in the as-synthesized state have a valence close to 3, as the edge energy matches closely with that of Mn_2O_3. It has also been shown by the extended X-ray absorption fine structure (EXAFS) analysis that the Mn ions are randomly distributed over the tetrahedral and octahedral metal ion sites within the spinel structure.

Fig. 1a showed the XANES spectra of Mn K-edge measured *in situ* during CV cycling. Upon CV cycling, the edge front was found to shifts toward lower energies during the cathodic sweep, while it moves back to pass over the OCV position and to higher energies during the anodic sweep. The results give direct evidence to the notion that charge-transfer takes place at the Mn-ion sites, balanced by Li insertion/extraction. In addition, the data may also indicate that the upper critical voltage limit (~4.5V) to the battery-like transformation corresponds to when the valence of Mn ions is about to exceed +3.

The reduction in Mn *k*-edge binding energy at the OCV state as compared with the as-synthesized state may indicate that part of the Mn ions are reduced when the cell was assembled. This reduction process apparently takes place in conjunction with insertion of Li ions into the oxide lattice, which thus enables the operation of the symmetric configuration, as shown later, where no Li electrode is involved. The nature of the oxidation counterpart has yet to be identified. It might involve oxidation of solvent species.

Fig. 1b showed the XANES spectra of Fe K-edge which was also measured *in situ* during CV cycling. First, it is found that the edge energies at the inflection point measured at voltages above 2.0V are almost the same. The valence of Fe ions is quite close to +3. Secondly, while the cell goes to the voltages below 2.0V, the edge front was found to shifts toward lower energies. But as it moves back to higher voltages, the edge energy showed that Fe ions can not recover the valence which indicated an irreversible reaction occurred. The capacitance also decays irreversibly at this situation and this may due to the valence change of Fe ions caused the structure instable.

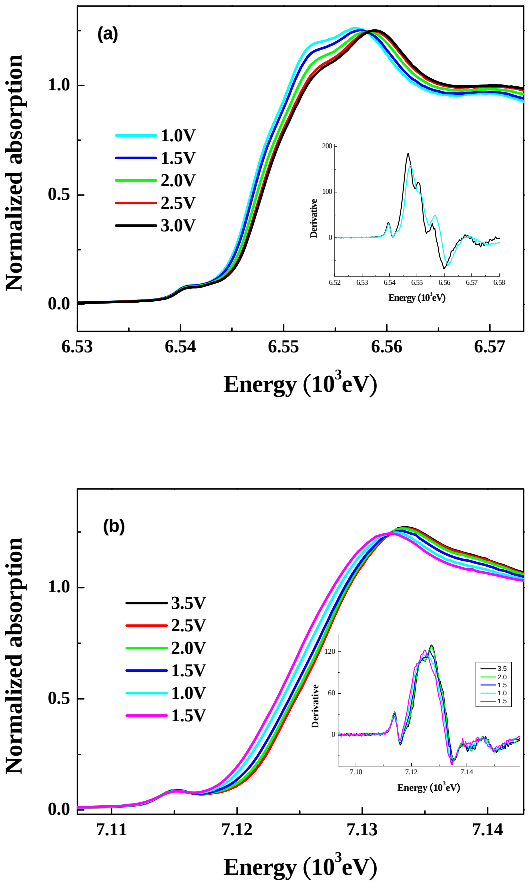

Figure 1. XANES data. (a) Curves of Mn K-edge acquired *in situ* during the charge (de-lithiation) phase at indicated voltages; and (b) curves of Fe K-edge acquired *in situ* during the charge-discharge phase at indicated voltages.