# In Situ X-ray Absorption Spectroscopic Studies of Anodically Deposited Binary Mn–Fe Mixed Oxides with Relevance to Pseudocapacitance

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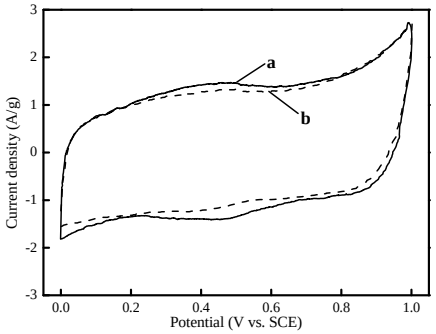
Mn/Fe binary oxides were successfully prepared on graphite substrates by anodic deposition. Atomic ratio of Mn/Fe can be simply controlled by adjusting the $FeCl_3$ addition in the 0.25 M $Mn(CH_3COO)_2$ plating solution.




Curves a and b in Figure 1 show the cyclic voltammetric behavior of Mn90Fe10 an Mn75Fe25 oxide, respectively. The results indicated that the oxide electrodes exhibited idea pseudo-capacitive performance and possessed the specific capacitances of 255 and 240 F/g, which were higher than that of the plain manganese oxide (205 F/g). Accordingly, the binary oxide materials are very promising for super-capacitor applications. Energy storage mechanism of the oxides is of great concern and examined by in situ X-ray absorption spectroscopy (XAS).

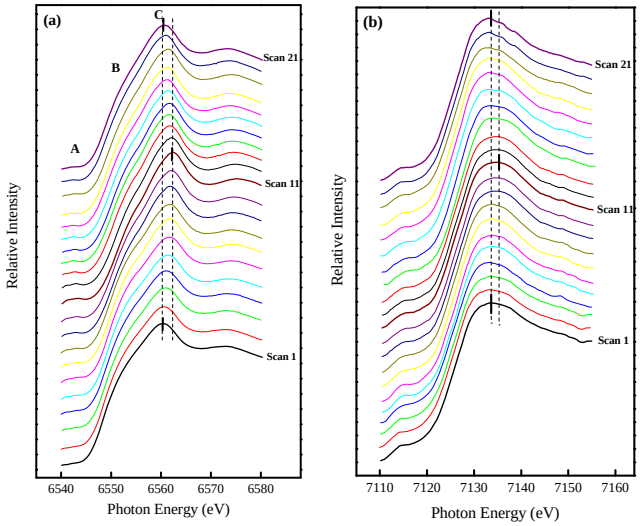



Figure 2 shows the XAS spectra of Mn90Fe10 oxide. For the experimental data of Mn K-edge, the adsorption edge (corresponding to oxidation state) gradually shifted toward higher energy with increasing applied potential and then backward lower energy as the potential was decreased. Similar phenomenon was also observed in the Fe K-edge spectra. The finding confirmed that the faradic redox reaction of Mn and Fe in the oxide electrode indeed occurred during the charge-discharge process.

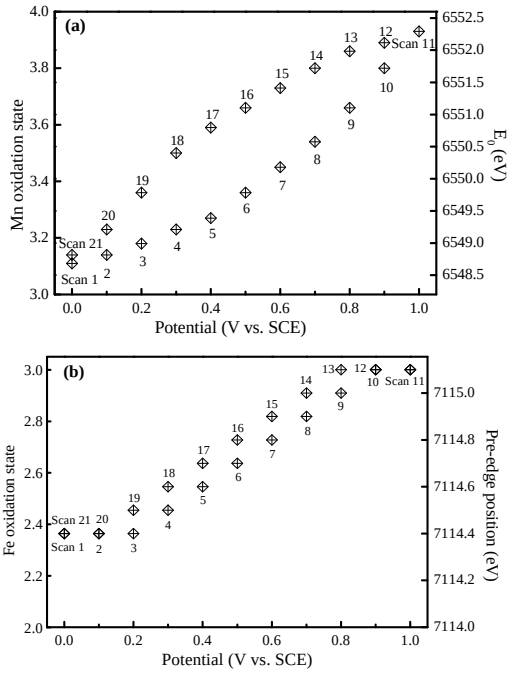



Figure 3(a) and 3(b) summarizes the Mn absorption threshold energy $E_0$ (obtained from the first inflection point on the main absorption edge) and Fe pre-edge energy and the corresponding oxidation state as a function of applied potential. The continuous and reversible change of Mn and Fe oxidation state with respect to potential was considered to contribute the pseudo-capacitive behavior as seen in Figure 1. Moreover, the variations of Mn and Fe oxidation state within 1 V were 0.81 and 0.55 for the Mn90Fe10 and Mn75Fe25 oxide, respectively. However, the average change in oxidation state per cation of the Mn90F10 oxide (0.78) larger than the Mn75Fe25 oxide (0.75) and plain Mn (0.70) The larger shift in the oxidation state well explained the higher specific capacitance of the former oxide electrode as demonstrated in Figure 1.