Insight into Pseudocapacitance Mechanism for Fe_3O_4/ Sulfite Supercapacitor

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Abstract

Searching for pseudo-capacitive material of low cost and environmental benignity has recently led us to discover nanocrystalline Fe_3O_4 supercapacitor based on aqueous electrolytes containing SO_3^{-2}. Although this system has been unequivocally shown to have an operation range of 1.1 V and a cycle life exceeding tens thousand cycles under low dissolved oxygen content (< 0.1 ppm), its specific capacitance varies dramatically, ranging from a few tens to greater than 300 F/g, with synthesis conditions. Understanding the pseudo-capacitance mechanism, which has not been revealed until now, is essential to the optimization of the performance of the device.

Investigation on the pseudo-capacitance mechanism was carried out in this work by using Fe_3O_4 thin film electrodes (Fig. 1) that were synthesized by electrodeposition on Pt foils. Electrochemical characterizations were conducted by using both cyclic voltammetry and EQCM (Electrochemical Quartz Crystal Microbalance) analyses (Fig. 2), in conjunction with structural and morphological analyses by XRD and SEM. For comparison, analyses were carried out not only in SO_3^{-2} electrolyte but also in other electrolytes, such as Cl^- and SO_4^{-2}, which give only electrical-double-layer capacitance. Experimental results point to the conclusion that the pseudo-capacitance results mainly from the SO_3^{-2}/S^{-2} redox couple involving the specifically adsorbed SO_3^{-2} surface species (Fig. 3). The roles of other surface reactions, such as the redox reactions of the oxide itself, on the performance of the supercapacitor are also identified.

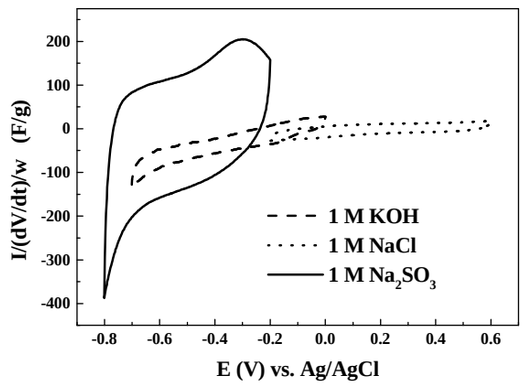

Fig. 1. CV of Fe_3O_4 thin film in different electrolyte solutions .

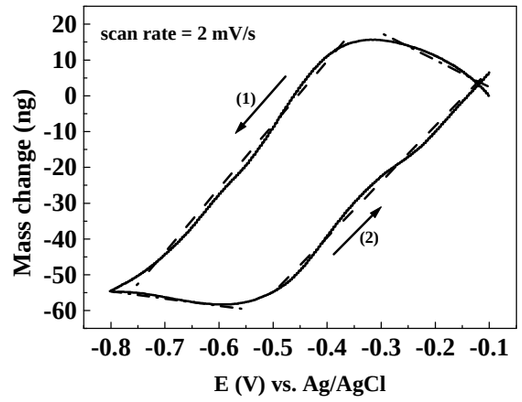

Fig. 2. EQCM analysis on Fe_3O_4 film in SO_3^{-2} electrolyte solution.

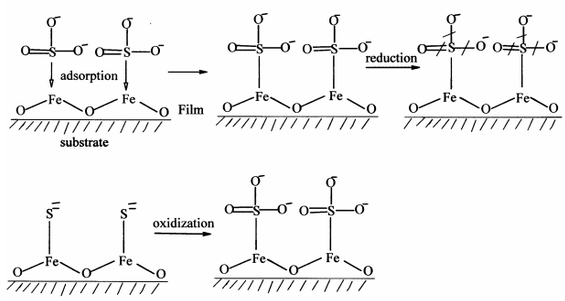

Fig. 3. Schematics of the proposed Pseudo-capacitance mechanism involving SO_3^{-2}/S^{-2} redox couple.