Electrochemical capacitor of magnetite in aqueous electrolytes

Nae-Lih Wu
Department of Chemical Engineering
National Taiwan University
Taipei, Taiwan 106, R.O.C.

The capacitive behaviors of magnetite nanocrystallites, along with conductive carbon black additive, in aqueous electrolytes, including sodium sulfite, sulfate, chloride, and phosphate, and potassium hydroxide, have been characterized. The behaviors can be categorized into three groups. Sodium sulfate and chloride electrolytes gave capacitances close to the space-charge capacitance of the oxide. Potassium hydroxide and sodium phosphate gave rise to a higher capacitance which can in part be attributed to surface redox reaction involving OH^-. Sodium sulfite resulted in the highest capacitances. In this electrolyte, the capacitance depends heavily on the dispersion of magnetite crystallites on the conductive matrix, and hence on the synthesis technique, ranging from a few tens to 510 F/g-Fe_3O_4 with an operation range of 1.1 V, based on a leakage current less than 0.1 mA F^{-1}. While the capacitance of the oxide was found to depend heavily on electrolyte composition, the self-discharge mechanism in these electrolytes appeared to be the same. Reduction in dissolved oxygen content (DOC) of electrolyte reduced leakage current and profoundly improved the cycling stability. In particular, in $Na_2SO_{3(aq)}$, the electrode showed no deterioration after 10^4 cycles under a DOC < 0.1 ppm.

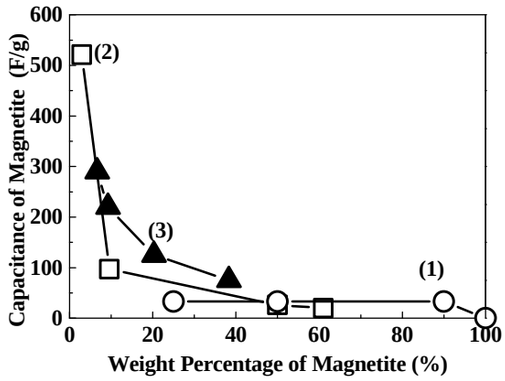

Figure 1. The dependence of the specific capacitance of magnetite on composition in magnetite/C composite electrodes synthesized by different methods, including (1) ex-situ physical mixing, (2) in-situ chemical precipitation, and (3) in-situ eletro-control release processes.

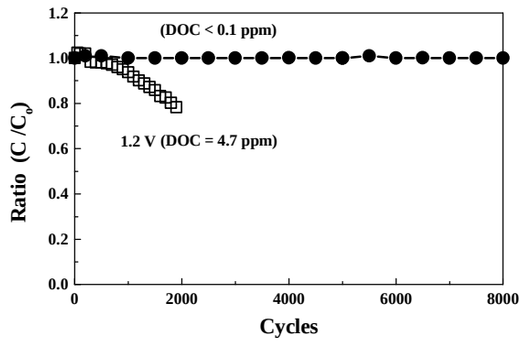

Figure 2. Cycling stability. C stands for capacitance, while the subscript “o” designates capacitance of the first cycle. (1 M $Na_2SO_{3(aq)}$; cycling voltage: 1.1 volt for the first 5000 cycles, and 1.2 V after.)