$FePO_4$-Carbon Composite Electrode for Calcium Rechargeable Battery Cathode

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Calcium rechargeable batteries have been attracted as one of multivalent ion batteries which are candidates for a post lithium ion battery. The calcium metal anode has a capacity of 1337 mAh g^{-1}, 2073 mAh cm^{-1} and the redox potential is almost the same as that of lithium metal. Therefore, rechargeable batteries using calcium metal anode have potential to become high energy density rechargeable batteries. In addition, calcium has a high melting point (842^{o}C) and it is abundant element, so that it is possible to realize high safety and low cost system. In recent years, the electrolyte that realizes the electrochemical dissolution and deposition of calcium metal has been reported [1]. However, to our knowledge, there are no reports of cathode active materials that calcium ions can be stably inserted and extracted. This is because increased interaction between cations and anions in the solid electrodes due to divalent character of calcium ions disturbs solid-state diffusion in the electrode. The shortening of diffusion length of calcium ion is accomplished by nano-sizing the active material. However, it leads to poor cycle characteristics because of its unstable nanostructure. In this research, we used a composite electrode where defective $FePO_4$ cathode active material of about 10 nm is highly dispersed in the carbon structure. This material exhibits very high rate characteristics against the insertion and extraction of lithium ions, and thus it is expected that the insertion and extraction reaction proceed even with divalent calcium ions.

The $FePO_4$-carbon composite was prepared by the "ultracentrifugation (UC)" method described elsewhere[2]. Electrode sheet obtained by mixing the carbon composite and PTFE at a weight ratio of 80:20 (wt%) was pressed on a Ti mesh to prepare an electrode. A three-electrode cell was fabricated with 0.5 M calcium bis (trifluoromethylsulfonyl) imide in acetonitrile as the electrolyte, Ag/Ag^+ double junction electrode as the reference electrode and an activated carbon sheet as the counter electrode.

Charge-discharge characteristics, rate characteristics and cycle characteristics of the electrode was measured at a voltage of upper limit 1.1 V, lower limit -1.0 V. As a result of the charge-discharge characteristic test, the discharge capacity was 174 mA h g^{-1} at a rate of 0.1 C and the potential of 0 V v.s. Ag/Ag^+. As a result of the rate characteristic tests, capacity in 5C was 92 mA h g^{-1}. The capacity retention after 85 cycles was 72%.

References:

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