

Magnesium Intercalation Host of Defective FePO₄-Carbon Composite

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Magnesium rechargeable batteries are expected as one of candidates for next generation rechargeable batteries. The advantages of magnesium metal anode are the high theoretical capacity, high reserve amount of magnesium metal, and no dendrite formation. However, divalent magnesium ions are difficult to diffuse in solid electrodes, and intercalation hosts that can operate at room temperature are limited to Chevrel structured compounds at present[1].

In this study, we investigated the applicability of FePO₄-carbon composite prepared by ultracentrifugation (UC) method as magnesium ion host structure. For nano-hybrid capacitor electrode, the electrode materials prepared by the UC method reported so far are capable of ultrafast lithium ion insertion and extraction reaction[2]. Therefore, magnesium ions could diffuse in the structure with a moderate condition. Since the irreversible magnesium ion insertion-extraction reaction in olivine type FePO₄ crystal has been reported[3], in this study, non-crystalline FePO₄ with carbon composite was used.

FePO₄-carbon composite was prepared by UC process[2]. The composite was mixed with PTFE. with the weight ratio of 9:1. The electrodes were charged using 1M LiPF₆ in a 3:7 volume ratio of ethylene carbonate and diethyl carbonate. The charged electrodes were washed with DME and then, three-electrode cell with an Ag⁺/Ag double junction reference electrode was constructed. The counter electrode was an active carbon, and the electrolyte was 0.5 M magnesium bis(trifluoromethanesulfonyl)imide in acetonitrile. Charge-discharge measurements were performed at 25°C. The valence state of Fe in the charged / discharged electrodes were examined by X-ray absorption spectroscopy, which was measured in a transmission mode.

Reversible charge / discharge capacity was observed after the first discharge. In operation at 25°C and a rate of 1/20 C, a capacity of 130 mAh/g and the potential of about 2 V versus magnesium metal are observed. From the TEM measurements, the structure of FePO₄ particles embedded in carbon and Mg intensity is observed only in regions where FePO₄ particles exist. Fe *K*-edge shifts downward in energy for the discharge reaction, reflecting the reduction of iron ions to maintain electrical neutrality upon magnesium-ion insertion in the discharge reaction.

References:

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