

LISICON-type Magnesium Iron Silicate as Cathode Material for Magnesium Ion Batteries

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Magnesium battery is a promising candidate for the next generation battery systems.¹ This battery however suffers from a low cell voltage and capacity. Much attention is inclined towards the positive electrode (cathode) as its performance is predominantly hampered by the aforementioned problems. Olivine-structured magnesium compounds are amongst viable cathode materials for magnesium battery, owing to their high theoretical capacity nearing 300 mAhg⁻¹.² The high capacity coupled with the high voltage in olivine-type magnesium compounds can bypass the bottlenecks of magnesium battery cathode materials. NuLi *et al.* synthesised MgMSiO₄ (where M = Fe, Mn or Co) and tested their charge-discharge properties.²⁻⁴ They showed a remarkably high discharge capacity of MgMSiO₄ at an average voltage of around 1.8 V versus magnesium. Ling *et al.* calculated the voltage for magnesium insertion/extraction in olivine-type MgMSiO₄ by the first-principle calculation.⁵ The reported voltages range from 2.0 V to 4.2 V versus magnesium, which are relatively higher than experimental voltages. Therefore, a higher voltage in conjunction with a high capacity can be anticipated, although the experimental reports remain unsatisfactory.²⁻⁴ In this study, we applied electrochemical ionic exchange from Li₂FeSiO₄ to MgFeSiO₄ to prepare a novel LISICON-type magnesium iron silicate as a cathode material for magnesium battery. We demonstrate for the first time a successful Li-Mg ionic exchange of Li₂FeSiO₄ nanoparticles to achieve a new MgFeSiO₄ framework exhibiting a reversible capacity exceeding 300 mAhg⁻¹ and at an average voltage of *ca.* 2.5 V vs. magnesium.

Li₂FeSiO₄/C was prepared via the solid state reaction. Stoichiometric amounts of Li₂CO₃, hydrated FeC₂O₄, and amorphous SiO₂ were mixed with carbon (10 wt %). The mixture was milled in a planetary ball mill (Fritsch P6) at 400 rpm for 24 hours. The precursor was pelletised and thereafter calcined at 800°C for 6 hours under Ar atmosphere. The XRD pattern of the pristine Li₂FeSiO₄ was fully indexed in the P2₁/n space group.⁶

Composite electrodes were fabricated with Li₂FeSiO₄/C, Ketjen black and PTFE in a 4:5:1 wt ratio. Two electrode flat cells (HS, Hosen) were assembled in an Ar-filled glove box. The counter electrode was lithium foil (Honjo) and the two electrodes were separated by separator (Celgard #2500). A 1M LiPF₆ in ethylene carbonate – ethyl methyl carbonate (3: 7 vol %) was used as electrolyte. All electrochemical measurements were performed at a constant current mode at 55°C. After the prepared cell was charged to 334 mAhg⁻¹ at C/50 rate, the cell was disassembled in an Ar-filled glove box. The

working electrode was washed with ethyl methyl carbonate and dried in vacuum. Three electrode cell was assembled by using this electrode with a platinum current collector. The counter electrode was magnesium rod and the reference electrode was a double junction Ag/Ag⁺ to prevent toxicity that can emanate from magnesium electrolyte. 0.5 M Mg-trifluoromethanesulfonyl-imide in acetonitrile was used as the electrolyte. Charge and discharge measurements were performed at 55°C. The charge-discharge rate was C/50. Charged or discharged electrodes were washed with acetonitrile and dried in vacuum. The samples were characterised using both X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD), taking caution not to expose the samples to air.

Figure 1 shows X-ray absorption near edge structure (XANES) at Fe K-edge of Mg_{1-x}FeSiO₄ during Mg²⁺ insertion in highly delithiated FeSiO₄ using Mg electrolyte. A diminution in the oxidation state of Fe causes a shift of the absorption edge towards lower energy. During discharge reaction, the absorption edge shifts towards lower energy indicating unambiguously that the charge compensation mechanism during Mg²⁺ insertion occurs via the change in oxidation state of Fe ion. This study shows the ability to use Li₂FeSiO₄ directly as a cathode in a Mg-ion battery cell.

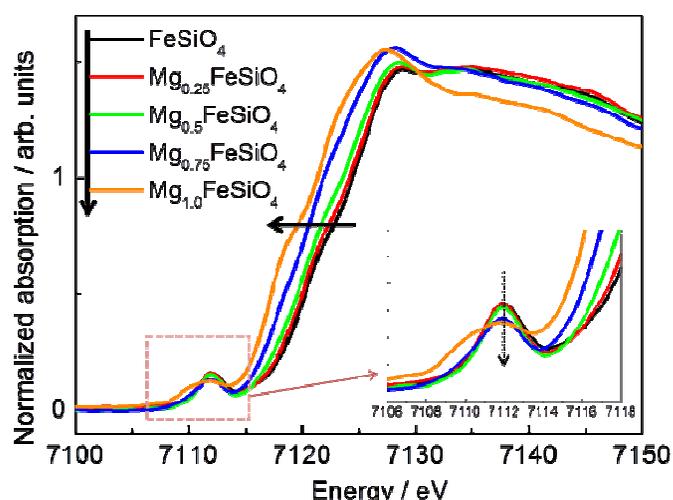


Fig.1 X-ray absorption near edge structure at Fe K-edge of Mg_{1-x}FeSiO₄ during Mg²⁺ insertion in highly delithiated 'FeSiO₄' using Mg electrolyte.

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