

Electrochemical Property and Structural Change of $\text{Li}_2\text{FeSiO}_4$ at Intermediate Temperature Using Molten LiTFSA-CsTFSA

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1. Introduction

Lithium metal orthosilicates (Li_2MSiO_4 , where $M = \text{Fe}, \text{Mn}$ and Co) have received prime attention as alternative cathode materials for Li-ion batteries beyond phosphate based electrode materials. In particular, the presence of two Li atoms per polyanion unit engenders a multielectron charge transfer (M^{4+}/M^{2+} redox couple), which is propitious for large-scale applications. Among this class of silicates, $\text{Li}_2\text{FeSiO}_4$ is reported to be an exciting intercalation host that is anticipated to vie with the stellar LiFePO_4 for prominence on the basis of its superior electrochemical properties, environmental benignity and low cost [1]. $\text{Li}_2\text{FeSiO}_4$ is a promising cathode material for the next-generation Li-ion battery owing to the high capacity that has recently been reported to be possible to achieve through modulation of the particle sizes [2]. In addition, it is thermally stable, whilst resources to prepare the material (*i.e.* Fe, (SiO_4)) are abundant in the Earth's crust and carry no safety risks. Despite its considerable advantages, $\text{Li}_2\text{FeSiO}_4$ is plagued with problems that have hindered its commercial deployment. Its key limitation is the poor rate performance presumably due to kinetically sluggish Li^+ kinetics within this material.

Molten salt is a liquid consisting of cation and anion. It has negligible volatility, nonflammability, high thermal stability, high electrochemical stability, and high ionic conductivity. So it is expected for electrolyte of batteries. Thermal and electrochemical property of MTFSA salts (TFSA = bis(trifluoromethylsulfonyl) amide, $M = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) and their mixture are reported and they have good property as electrolyte of batteries[3, 4]. In addition, this electrolyte can be used at intermediate temperature. This study investigates rate capability of $\text{Li}_2\text{FeSiO}_4$ operating at intermediate temperature condition.

2. Experimental

$\text{Li}_2\text{FeSiO}_4$ were prepared via a facile solid state reaction method at 1073 K under argon atmosphere. The crystal structure and morphology of the pristine $\text{Li}_2\text{FeSiO}_4$ powders were characterized by XRD, SEM, TEM and elemental carbon analysis.

Charge and discharge tests at room temperature were performed by using coin cell-type batteries. 1 M LiPF_6 in EC: EMC solution (molar ratio 3:7) was used as the electrolyte. Reference and counter electrodes were Li foils. Charge and discharge tests at intermediate temperature (433 K) were performed by using two-electrode cell. Molten LiTFSA-CsTFSA (molar ratio 2:8) was used as the electrolyte. LiTFSA and CsTFSA are purchased and dried under vacuum at 473 K and 373 K for 12 h before measurement. Reference and counter

electrodes were Li foils.

3. Results and discussion

Figure 1 shows charge-discharge curves of $\text{Li}_2\text{FeSiO}_4$ at room temperature. The initial charge profile is different from second charge curve, a phenomenon which has been ascribed to structural rearrangements. According to XRD measurement, the phase transformation was hardly observed upon initial charging process at high rates, whilst the complete phase transformation was only observed on charging at low rates [5]. Figure 2 shows charge discharge curves of $\text{Li}_2\text{FeSiO}_4$ at intermediate temperature. Different from room temperature, plateau appeared at initial charge, and high rate charge discharge (1 C) is possible. It indicates that structural rearrangement occurs quickly at intermediate temperature.

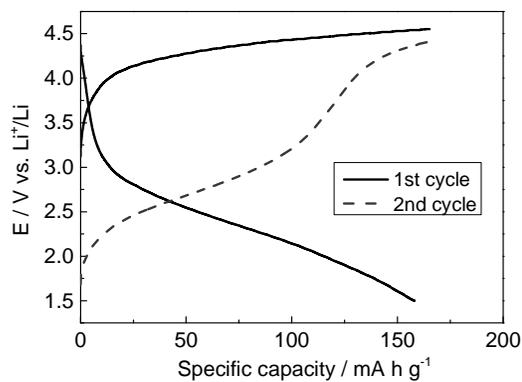


Fig. 1 Charge-discharge curves of the Li/1 M LiPF_6 in EC:EMC(3:7)/ $\text{Li}_2\text{FeSiO}_4$ cell at 298 K (1.5 – 4.5 V, constant current at C/10).

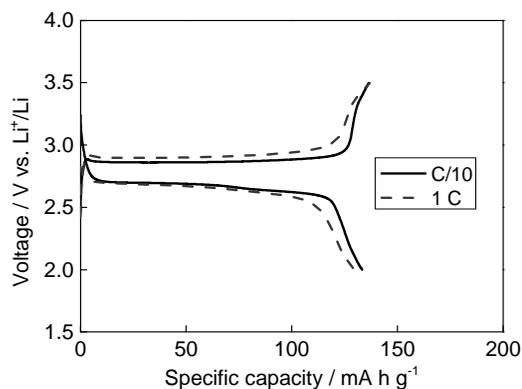


Fig. 2 Charge-discharge curves of the Li/(Li₂₀,Cs₈₀)TFSA/ $\text{Li}_2\text{FeSiO}_4$ cell at 433 K (2.0 – 3.5 V, constant current at 1 C, C/10).

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