

Two-electron migration orthosilicate cathode material for Na-ion batteries

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Experimental

The synthesis of carbon-coated $\text{Li}_2\text{FeSiO}_4$ nanoparticles: $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite was synthesized by a modified sol-gel method.^{9b} Typically, 2 g triblock copolymer Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) was dissolved in 50 ml absolute alcohol. 8 mmol of lithium acetate, 4 mmol of ferric nitrate and 4 mmol of tetraethyl orthosilicate (TEOS, CP) were added into the alcohol solution of P123 in sequence with vigorous magnetic stir until the substances added were completely dissolved. After that, the solution was heated at 70°C with simultaneous stirring until the alcohol was completely evaporated. Homogeneous and brownish slurry with a certain viscosity could be obtained during the alcohol evaporation process. Finally when all the alcohol was vaporized, the dried mixture was grounded into powder and calcinated at 600°C for 10 hours in a tube under Ar flow. After cooling to room temperature, a black product was obtained.

The synthesis of $\text{Li}_2\text{FeSiO}_4/\text{C}$ -graphene composite: To avoid segregation, the

carbon-coated $\text{Li}_2\text{FeSiO}_4$ nanoparticles were ball-milled for 2 h (with a velocity of 500 r/min). The nanoparticles were then dispersed in deionized water by magnetic stirring with a content of 50 wt.%. Graphite oxide was prepared using the traditional Hummers' method.¹¹ By simply ultrasonic treatment of synthesized graphite oxide, graphene oxide (GO) nanosheets could be obtained, which was then dispersed in deionized water with a concentration of 2 mg/mL. To prepare the $\text{Li}_2\text{FeSiO}_4/\text{C}$ -graphene composite, GO dispersion was added into the $\text{Li}_2\text{FeSiO}_4$ nanoparticles dispersion under vigorous stir, forming a slurry with the weight ratio of $\text{Li}_2\text{FeSiO}_4/\text{C}$ to GO as 2:1. After simultaneous stirring and drying at 80°C for 1 h, the slurry became solid powder, which was then annealed at 350°C for 4 h in an Ar flow. Final product in black color could be obtained when the furnace tube was cooled to room temperature.

Materials Characterization: The crystal structural characterization of the samples was carried out on a Bruker D8 Advance X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm). The morphologies of the composites were investigated using a field-emission scanning electron microscope (SIRION, FEI, USA). Transmission electron microscope (TEM) images and high-resolution transmission electron microscope (HRTEM) images were taken on a JEM 2010-FEF (JEOL Ltd., Japan) operating at 200kV. The carbon content in the composite was determined by VarioEL III elemental analyzer ((Elementar Analysen System GmbH, Germany).

Delithiation and sodiation processes: The electrochemical delithiation of $\text{Li}_2\text{FeSiO}_4$ was carried out in coin type R-2032 half cells using lithium metal disks as

anodes, Celgard 2300 microporous films as separators, and 1 M LiPF_6 in a 1:1 volumetric mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as electrolyte. The $\text{Li}_2\text{FeSiO}_4$ electrode film was fabricated using a mixture of the synthesized $\text{Li}_2\text{FeSiO}_4/\text{C}$ -graphene composites, acetylene black (AB), and polytetrafluoroethylene (PTFE) in N-methylpyrrolidone with a weight ratio of 80:15:5. The resulting slurry was cast onto Al mesh, dried at 110 °C under vacuum for overnight. The cells were then assembled in Ar-filled glove box. Generally the weight of composite materials in each cathode film varied between 4.0 and 6.0 mg. The Li half cells were galvanostatically charged at a current (10 mA g^{-1} , 20 mA g^{-1} and 50 mA g^{-1} , respectively) to 4.8 V. In order to make sure that the $\text{Li}_2\text{FeSiO}_4/\text{C}$ -graphene composites were delithiated as much as possible, the cells were generally charged and discharged between 1.5 V and 4.8 V for a whole cycle before they finally charged back to 4.8 V.

The cells were then disassembled and the cathodes were washed thoroughly in DEC in Ar-filled glove box. The cathodes were then transferred to R-2032 type coin cells using Na metals as anodes, glass fibers as separators, and 1 M NaClO_4 dissolved in the propylene carbonate (PC) electrolyte. The Na half cells were galvanostatically discharged and charged between the voltages of 1.2 V to 4.5 V in order to make sure that the delithiation and sodiation were progressed in the same voltage window.

For all the cells the applied currents and the resulting capacities were calculated based on the weight of the pristine $\text{Li}_2\text{FeSiO}_4$ material if not specified.

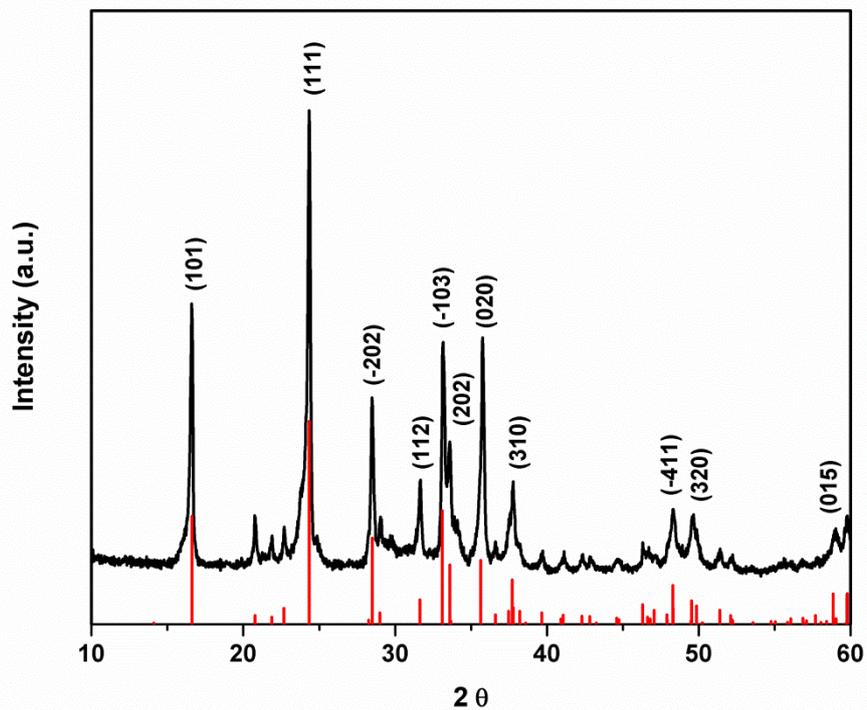


Fig. S1 The XRD pattern of the synthesized $\text{Li}_2\text{FeSiO}_4/\text{C}/\text{Graphene}$ composite. All the reflection peaks can be indexed on the basis of the monoclinic $P2_1$ phase $\text{Li}_2\text{FeSiO}_4$ without any reflection peak from impurities.

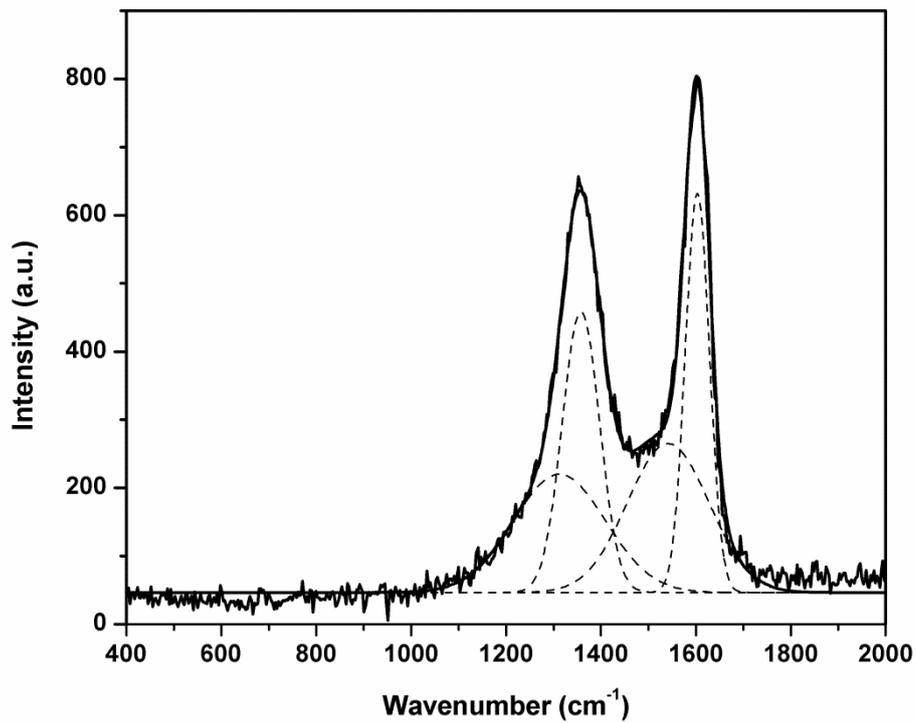


Fig. S2 The Raman spectrum of the synthesized $\text{Li}_2\text{FeSiO}_4/\text{C}/\text{Graphene}$ composite.

The spectrum can be deconvoluted into four Gaussian bands, with the peaks at 1355 and 1606 cm^{-1} corresponding to the fundamental D and G bands of carbons respectively.

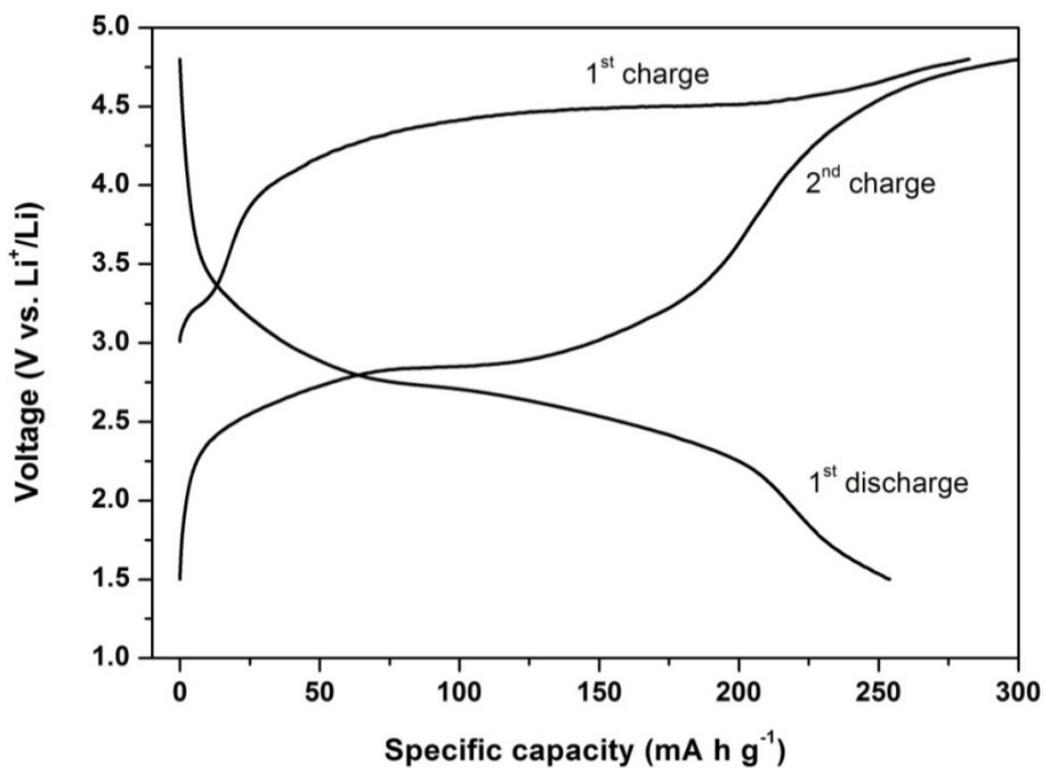


Fig. S3 The charge-discharge curves of the $\text{Li}_2\text{FeSiO}_4/\text{Li}$ cells. The second charge process of the cell is the delithiation of $\text{Li}_2\text{FeSiO}_4$ cathode material in the experiment. Before the delithiation, the cell is generally charge-discharged for a whole cycle.

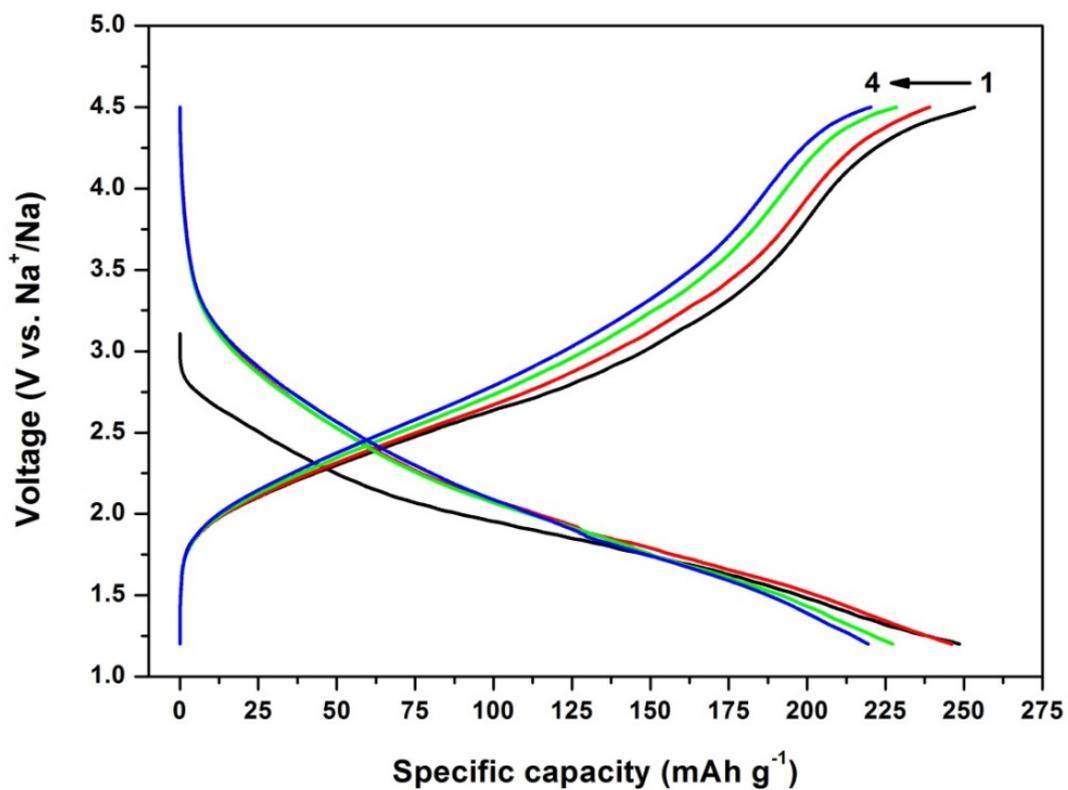


Fig. S4 The charge-discharge curves of the initial 4 cycles for the Na cells, with the sodium iron orthosilicate obtained as the cathode material, at the rate of 20 mA g⁻¹ at room temperature.