

Enhanced Electrochemical Performance of Cd-Modified $\text{Li}_2\text{FeSiO}_4/\text{C}$ Cathode Material for Lithium-ion Batteries

Song Duan[†], Lu-Lu Zhang^{†,*}, Gan Liang[‡],

Xue-Lin Yang^{†,*}, Shi-Bing Ni[†], Ming Li[†], Gang Peng[†]

[†]College of Mechanical and Material Engineering, Three Gorges University, 8 Daxue Road, Yichang, Hubei 443002, China

[‡]Department of Physics, Sam Houston State University, Huntsville, Texas 77341, USA

Introduction

Recently, as a new kind of polyanion cathode materials for lithium ion batteries, $\text{Li}_2\text{FeSiO}_4$ has attracted much attention due to the abundant and inexpensive raw materials, nontoxicity, high safety, and high theoretical capacity (332 mA h g^{-1})^{1,2}. However, as the intrinsic characteristics of polyanionic materials, $\text{Li}_2\text{FeSiO}_4$ suffers from poor electronic conductivity and slow lithium ion diffusion, which limits its practical application in lithium-ion batteries³. Fortunately, the electrochemical performance of $\text{Li}_2\text{FeSiO}_4$ can be enhanced by many methods, such as carbon coating⁴, cation incorporation⁵, and particle size reduction⁶. Up to now, there is no report about Cd modification for $\text{Li}_2\text{FeSiO}_4$. Here, Cd-modified $\text{Li}_2\text{FeSiO}_4/\text{C}$ cathode material was synthesized via a solid-state reaction assisted with refluxing, and the effect of Cd on the physicochemical and electrochemical performance of $\text{Li}_2\text{FeSiO}_4/\text{C}$ was also investigated.

Experimental

$\text{Li}_2\text{FeSiO}_4/\text{C}$ composite was synthesized by a solid-state reaction assisted with refluxing. Lithium acetate, ferrous oxalate, and tetraethyl orthosilicate (TEOS) were successively dissolved in ethanol, and then heated at 80 °C for 24 h. After evaporating (ethanol) and vacuum drying, the obtained dry gel was mixed with a certain amount of sucrose in acetone by ball-milling. The resulting precursor was dried at 50 °C, and then calcined at 350 °C for 5 h, followed by 650 °C for 10 h in N_2 . To obtain Cd-modified $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite, $\text{Li}_2\text{FeSiO}_4/\text{C}$ particles were dispersed in a solution containing cadmium acetate by ultrasonic method, and then the above mixture was stirred by a magnetic force stirrer until dry. Subsequently, the precursor was calcined at 600 °C for 5 h in N_2 .

The working electrodes were prepared by mixing the prepared cathode materials (i.e., $\text{Li}_2\text{FeSiO}_4/\text{C}$ and Cd-modified $\text{Li}_2\text{FeSiO}_4/\text{C}$) with PVDF and acetylene black in a weight ratio of 75:15:10 in N-methyl pyrrolidinone solvent. Lithium foil was used as counter and reference electrodes. A solution of 1 mol/L LiPF_6 in EC/DMC (LB-301, China) was employed as the electrolyte. Electrochemical measurements were carried out between 1.5–4.6 V vs. Li^+/Li^0 with CR2025 coin cells.

Results and Discussion

Fig. 1 shows the XRD patterns of the pristine $\text{Li}_2\text{FeSiO}_4/\text{C}$ and Cd-modified $\text{Li}_2\text{FeSiO}_4/\text{C}$ powders. Though some impurities were detected, the main diffraction peaks not only for the pristine $\text{Li}_2\text{FeSiO}_4/\text{C}$ composite but also for the Cd-modified $\text{Li}_2\text{FeSiO}_4/\text{C}$ sample are well indexed as the monoclinic $\text{Li}_2\text{FeSiO}_4$ with a space group of $\text{P}2_1/n$, which indicates that Cd-incorporation does not change the crystal structure of $\text{Li}_2\text{FeSiO}_4$. Noting that, no diffraction peaks from carbon are observed, indicating that the pyrolytic carbon from sucrose is in amorphous form or its content is too low to be detected.

Fig. 2 shows the cycling performance at a current density of 0.1 C and the rate capability of $\text{Li}_2\text{FeSiO}_4/\text{C}$ and Cd-modified $\text{Li}_2\text{FeSiO}_4/\text{C}$ electrodes. The rate capability was tested in a mode such that all cells were charged under a small current density of 0.1 C to 4.6 V

and discharged at different rates to 1.5 V. Compared to the pristine $\text{Li}_2\text{FeSiO}_4/\text{C}$ electrode, the Cd-modified $\text{Li}_2\text{FeSiO}_4/\text{C}$ delivers a higher initial discharge capacity of 191.3 mAh g^{-1} and still retains a capacity of 173.3 mAh g^{-1} even after 50 cycles. As shown in Fig. 2b, in all cases, the Cd-modified $\text{Li}_2\text{FeSiO}_4/\text{C}$ electrode exhibits much higher capacity than the pristine $\text{Li}_2\text{FeSiO}_4/\text{C}$. Obviously, Cd-modified $\text{Li}_2\text{FeSiO}_4/\text{C}$ shows better electrochemical performance than $\text{Li}_2\text{FeSiO}_4/\text{C}$.

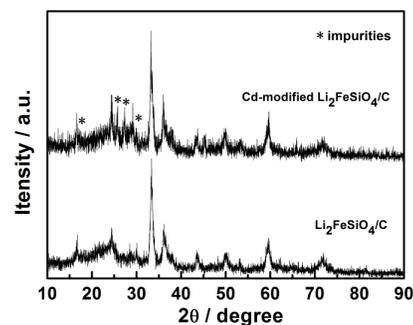


Fig. 1 XRD patterns of $\text{Li}_2\text{FeSiO}_4/\text{C}$ and Cd-modified $\text{Li}_2\text{FeSiO}_4/\text{C}$ powders

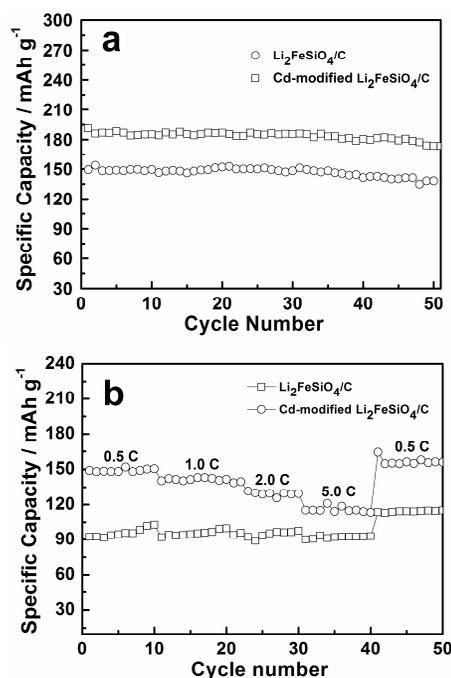


Fig. 2 (a) The cycling performance at 0.1 C, and (b) the rate capability of the two as-obtained samples.

Acknowledgements

This work was financially supported by Natural Science Foundation of China (NSFC, 51272128), Excellent Youth Foundation of Hubei Scientific Committee (2011CDA093), and Key Project of Hubei Provincial Department of Education (No. D20131303). Moreover, the authors are grateful to Dr. Jianlin Li at Three Gorges University for his kind support to our research.

References

1. A. Nýtén, A. Abouimrane, M. Armand, T. Gustafson, J.O. Thomas, *Electrochem. Commun.* **7** (2005) 156.
2. Z. Yan, S. Cai, X. Zhou, Y. Zhao, L. Miao, J. Electrochem. Soc. **159** (2012) A894.
3. Z.M. Zheng, Y. Wang, A. Zhang, T.R. Zhang, F.Y. Cheng, Z.L. Tao, J. Chen, *J. Power Sources* **198** (2012) 229.
4. G. Peng, L.L. Zhang, X.L. Yang, S. Duan, G. Liang, Y.H. Huang, *J. Alloys Comp.* **570** (2013) 1.
5. R. Chen, R. Heinzmann, S. Mangold, V.S. Kiran Chakravadhanula, H. Hahn, Sylvio Indris, *J. Phys. Chem. C* **117** (2013) 884.
6. X. Huang, H. Chen, S. Zhou, Y. Chen, J. Yang, Y. Ren, H. Wang, M. Qu, Z. Pan, Z. Yu, *Electrochim. Acta* **60** (2012) 239.