

RAPID COMMUNICATION

Energy storage in composites of a redox couple host and a lithium ion host

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Received 16 February 2012; received in revised form 10 April 2012; accepted 21 April 2012 Available online 22 May 2012

KEYWORDS

Energy storage; Li -ion batteries; Electrochemistry; Positive electrode; Composite materials **Abstract** The quest for new positive electrodes for rechargeable lithium-ion batteries has been escalating in recent years. Until now, candidates of positive electrode were limited to crystals that contain both redox-active element (usually transition-metal) and lithium ion in the open framework with few exceptions. Here, we demonstrate lithium-free compounds, a material with little activity by itself, can be activated electrochemically by addition of LiF after the first charging. This general strategy is exemplified in various lithium-free iron compounds. Reversible lithium ion extraction and reinsertion take place for Fe²⁺F₂, Fe²⁺SO₄, and Fe₂²⁺P₂O₇, when blended with LiF in nanoscale, in which a simultaneous valence change of Fe^{2+/3+} occurs above 3 V. FeF₂–LiF could deliver 190 mAh g⁻¹ (~3.53 V) at 50 mA g⁻¹ which is even higher energy density than that crystalline LiFePO₄ can offer. Various combinations of blending are possible using this approach, which can bring a new branch of material group for positive electrodes in lithium-ion batteries.

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Current Li-ion battery technology faces challenges with regard to energy/power density, cycle life, production cost, and safety when used in emerging applications, such as electric vehicles and large scale energy backups [1-5]. The

performance of Li-ion batteries is mainly determined by the electrode materials, hence the quest for better electrode materials has never been higher. However, the discovery of new positive electrodes is significantly restricted because only a small number of Li-containing material groups are practically considered for current Li-ion battery systems. There are only limited choices of materials that contain Li and a redox-active transition metal (preferably light 3d metals) within an open anion framework [2]. Meanwhile, several Li-free materials have been studied as positive electrodes vs. elemental Li in a 'half-cell' such as FeF₃, FePO₄, V_2O_5 , and BiF₂ [6–11]. Although some showed excellent

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^{1748-0132/\$ —} see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.nantod.2012.04.004

electrochemical performance in the 'half-cell', they are not practical for application in Li-ion batteries. Generally, the positive electrodes donate Li ions because metallic Li and Li-containing negative electrode materials are unfavorable due to the safety concern and chemical instability [2].

Here, we suggest a novel strategy to use Li-free transition metal ionic compounds (MX, M = transition metal, X = anion or polyanion group) as an active positive electrode for Li-ion batteries. MX is blended with a simple Li ionic compound (LiY, Y = anion or polyanion group) in nanoscale. In this nanocomposite electrode, MX provides a redox couple for an electrochemical reaction, while Li jons are supplied from LiY. Unlike conventional positive electrodes in which transition metal ions and Li ions reside in the same crystal domain (Fig. 1a), transition metal ions and Li ions in the nanocomposite are spatially separated at the nanoscale into two different crystal domains of MX and LiY, respectively (Fig. 1b). This spatial separation of the Li source and electron source may lead to concerns about whether the composite electrode would be electrochemically active. However, recent ground-breaking studies have revealed that nanocomposites of a metal (M) and a Li compound (LiX) could reversibly store and release Li ions through a conversion reaction (MX + Li \leftrightarrow M + LiX) [12–14]. Nevertheless, the following questions still remain.

- (i) Will the reversible electrochemical reaction still occur for a nanocomposite of a transition metal ionic compound (MX) and a Li ionic compound (LiY)?
- (ii) If so, will the reaction mechanism be similar to the conversion reaction $(MX + LiY \leftrightarrow MXY + Li \text{ or } MX + LiY \leftrightarrow MX + Li + Y)$?



Fig. 1 Schematic illustration of the crystal structures of (a) a conventional positive electrode (*e.g.*, $LiCoO_2$) and (b) a suggested composite positive electrode (*e.g.*, FeF_2 -LiF composite) (green: Li, brown: Co/Fe, red: O, gray: F).

(iii) Will major structural reconstitution occur for MX during an electrochemical reaction, similar to the conversion reaction in which MX is converted to a different M crystal structure?

In this work, we show that reversible Li extraction/insertion does occur for MX—LiY nanocomposites, but not via a conventional conversion reaction mechanism. Once Li ions are extracted from LiY, MX immediately forms a new MXY compound that can reversibly host Li ions. Because further Li insertion/extraction reactions occur via



Fig. 2 (a) XRD patterns of FeF₂ (black), LiF (red), and FeF₂-LiF composite (blue), (b) high-resolution TEM image of FeF₂-LiF composite, charge-discharge profiles of FeF₂-LiF composite in (c) a half-cell and in (d) a full-cell at 50 mA g⁻¹.



Fig. 3 XAS analysis of Fe-K edge in FeF_2 -LiF composite electrode: (a) XANES spectra and (b) FTs of EXAFS spectra in comparison with standard FeF_2 (cyan) and FeF_3 (magenta) (black: as-prepared electrode, red: charged electrode, blue: discharged (cycled) electrode).

intercalation in the host MXY that do not involve major structural reconstitution, large polarization (or hysteresis), a commonly observed drawback of conversion reaction electrodes, is not observed after the first charge process.

As a proof of concept, we chose nanocomposites of LiF and Fe-containing compounds, because Fe-based electrodes offer several advantages, such as low cost and environmental benignity [15,16]. A FeF₂—LiF nanocomposite electrode was the first to be examined. The composition of the nanocomposite FeF₂—LiF was identical to the lithiated form of FeF₃ (LiFeF₃). FeF₃ has been studied for its high specific capacity (237.51 mAh g⁻¹) and high thermal stability [6,7,17–19]. However, the FeF₃ electrode does not inherently contain Li ions; therefore, it was excluded as a positive electrode for Li-ion batteries. To the best of our knowledge, LiFeF₃ does not exist in nature, and the synthesis of LiFeF₃ has not been reported.

FeF₂-LiF nanocomposite was fabricated from planetary millings (Fig. 2a and Supporting Information S1). Detailed description in experiments is in Supporting Information. Fig. 2b shows that the FeF₂-LiF composite was composed of nanocrystallites less than 5 nm in diameter. To examine the feasibility of the FeF2-LiF nanocomposite as a positive electrode, an electrochemical test was first performed in a half cell (Fig. 2c). Interestingly, reversible charge and discharge occurred for the nanocomposite electrode with a high capacity value (ca. 190 mAh g^{-1}). However, the first charge process resulted in a significantly different profile compared to those of subsequent charge-discharge cycles. This strongly implies that the Li extraction reaction in the first cycle differed from that in subsequent cycles. After the first charge, the following cycles showed no change in the shape of the charge and discharge profiles. Because voltage hysteresis is closely related to major structural reconstitution during a conversion reaction, it is unlikely that FeF2-LiF was

involved in the major structural reconstitution during cycles after the first charge [17]. The high specific capacity of the FeF2-LiF composite was impressively well retained upon prolonged cycle testing (Supporting Fig. S2). While FeF₂-LiF performed successfully as a positive electrode in the halfcell, further investigation was needed to determine whether it functions similarly in a full-cell using a Li-free carbon negative electrode. Fig. 2d shows the charge-discharge profiles of the full-cell consisting of the carbon negative electrode and the FeF2-LiF composite positive electrode after the initial activation cycle. The operation voltage of the full-cell was lower than that of the half-cell because of the excess carbon negative electrode that initially exhibited a high potential (positive electrode/negative electrode = 1/15 in weight). The discharge capacity was approximately 165 mAh g^{-1} . While further optimization of a full-cell is required, such as an electrode balancing, the feasibility of a FeF2-LiF nanocomposite electrode in a full-cell was confirmed, indicating that our strategy can be successfully applied to the current Li-ion battery cell assembly.

To explain this surprising behavior of the FeF₂–LiF electrode, we carefully examined the reaction mechanism of the FeF₂–LiF electrode. Among several possibilities including side reactions, we conclude the electrochemical reaction occurred mainly by the FeF₂–LiF electrode (Supporting Information S3). X-ray absorption spectroscopy (XAS) was carried out on the electrode in various states. Firstly, we monitored the oxidation state of Fe ions. Fig. 3a compares the Fe K-edge X-ray absorption near edge structure (XANES) spectra for the electrodes in the three different states. It was clear that the entire Fe K-edge shifted toward higher energy when charged, indicating that Fe²⁺ in FeF₂–LiF was oxidized to Fe³⁺. Upon discharge, the Fe K-edge shifted back to lower energy. This confirmed that the Fe^{2+/3+} redox couple was active during Li extraction (charge) and

insertion (discharge) of FeF₂–LiF. An independent X-ray photoelectron spectroscopy (XPS) study also supports the Fe^{2+/3+} redox reaction (Supporting Fig. S4a). Secondly, reversible Li storage was identified. The XPS spectra of Li_{1s} suggest that Li was removed during charging and restored during discharging (Supporting Fig. S4b). X-ray diffraction (XRD) study revealed the decomposition of LiF after charge, however, the decomposed LiF was not recovered after discharge, indicating that decomposition of LiF is irreversible (Supporting Information S4c).

Once Li ions were extracted from LiF (as observed) and moved to the negative electrode during charging, one should naturally wonder where the fluorine ions remain. Also, it would be very surprising if Fe^{2+} was oxidized to Fe^{3+} in FeF_2 . These puzzles may be solved through a hypothesis that the unpaired fluorine ions may combine with Fe²⁺F₂ to form a $Fe^{3+}F_3$ -like phase. This hypothesis is viable because, in a conversion reaction of M+LiX, the extraction of Li from LiX results in the simultaneous formation of an MX compound [20,21]. To clearly view the change in local atomic environments in the FeF2-LiF nanocomposite, an extended X-ray absorption fine structure (EXAFS) study was carried out in comparison with the standard rutile FeF₂ and trigonal FeF₃ samples. Detailed description on EXAFS fitting is in Supporting Information S5. Fig. 3b shows that FeF₂ in the as-prepared nanocomposite electrode was well matched with the standard rutile FeF₂ model, as expected. However, upon charging the electrode, the Fourier transforms (FTs) of EXAFS spectra deviated notably from the standard FeF₂ character, indicating that a change occurred in the local atomic structure of FeF₂. The increased intensity and slightly reduced position in the distance of the first peak (A), corresponding to a Fe-F bond in the FeF_6 octahedra, strongly suggests the formation of a trigonal FeF₃-like phase. However, the first Fe-F (A) peak intensity of the charged electrode was relatively small compared to that of the trigonal FeF₃ standard, suggesting the formation of a defective FeF₃ structure with a likely fluorine deficiency. Fluorine ions are believed to have been incorporated into FeF_2 by binding with Fe in the crystal. This agrees with the hypothesis that FeF₂ in the composite transformed to a FeF₃-like phase after the initial charge. FT of the EXAFS spectrum of the discharged electrode shows analogous features with that of the pristine rutile FeF₂. This implies that Li insertion into the trigonal FeF₃-like phase resulted in the formation of a trirutile Li_xFeF₃ phase. The transformation from trigonal FeF₃ to trirutile Li_xFeF₃ is consistent with previous results that revealed a phase transformation of FeF₃ from the trigonal to a trirutile during an electrochemical reaction [17,18]. In general, the local Fe-F and Fe-Fe environments in rutile FeF₂ and trirutile Li_xFeF₃ are similar, resulting in analogous FTs of the EXAFS spectra [17,18]. By combining the analysis results, the reaction mechanism of the FeF2-LiF composite can be summarized as follows.

$$Fe^{2+}F_2 + LiF \rightarrow Fe^{3+}F_3 + Li^+ + e^- \leftrightarrow LiFe^{2+}F_3$$
(1)

Briefly illustrated in Fig. 4.

During the first charge, LiF decomposed to Li ions and fluorine ions. The fluorine ions were immediately incorporated into FeF_2 to form a FeF_3 , oxidizing Fe^{2+} to Fe^{3+} in the nanocomposite. During the subsequent discharging



Fig. 4 Schematic illustration of the proposed electrochemical reaction mechanism of the FeF_2 -LiF composite (green: Li, brown: Fe, gray: F).

and charging, the new FeF_3 host allowed the reversible Li ion intercalation. In situ formation of metal fluorides from M—LiF nanocomposite has been previously reported [20,21]. However, the novelty aspect here is the reaction between a metal fluoride compound and LiF to form a higher oxidation state compound *in situ*.

The general suitability of the suggested new mechanism was examined with two additional Fe-based nanocomposites, FeSO₄-LiF and Fe₂P₂O₇-LiF. A reversible electrochemical reaction in both composites takes place (Supporting Information S6), which strongly suggests that our strategy can be applied to various materials systems. Interestingly, the average voltages between charge and discharge of the composites varied for the same $Fe^{2+/3+}$ redox couple depending on the anion group of the Fe-containing compounds (3.53 V in FeF2-LiF, 3.29 V in FeSO₄-LiF, and 3.21 V in Fe₂P₂O₇-LiF). Furthermore, we show that Mn₂P₂O₇-LiF is also electrochemically active with higher voltage of 4.0V (Supporting Information S7). This suggests that the operation voltage of the nanocomposite electrode can be tuned by selecting X and M in MX of the nanocomposite.

In summary, we proposed a novel strategy to use Li-free materials as positive electrodes for Li-ion batteries. Composite materials composed of a redox couple host (MX) and a Li ion host (LiY), such as FeF_2 —LiF nanocomposites, were shown to be electrochemically active with a new mechanism. Our approach can be extensively applied to other nanocomposites with a metal host and Li host, as demonstrated for $FeSO_4$ —LiF, $Fe_2P_2O_7$ —LiF and $Mn_2P_2O_7$ —LiF. We believe that material selection of the positive electrode can be extended beyond the boundary of Li-containing materials by using nanocomposite as positive electrode. Because the combination of composites is infinite, this strategy can open up a new branch of material group for positive electrodes.

Acknowledgements

This work was supported by Energy Efficiency and Resources R&D program (20112020100070) under the Ministry of Knowledge Economy, Republic of Korea. This work was also supported by Human Resources Development of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy (20114010203120) and by the Converging Research Center Program through the Ministry of Education, Science and Technology (2011K000691). The work at BNL was supported by the Northeastern Center for Chemical Energy Storage, and Energy Frontier Research Center funded by the U.S. DOE, BES under award No. DE-SC0001294. The authors would like to express their gratitude to Professor Glen. G. Amatucci for his valuable discussion in this work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.nantod.2012.04.004.

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