

Discovering a Novel Sodiation in FeF₂ Electrodes for Sodium-Ion Batteries

Kai He¹, Peng Gao², Nathalie Pereira³, Glenn G. Amatucci³, Yimei Zhu⁴, Feng Wang² and Dong Su¹

¹. Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973

². Sustainable Energy Technologies Department, Brookhaven National Laboratory, Upton, NY 11973

³. Department of Materials Science and Engineering, Rutgers University, North Brunswick, NJ 08902

⁴. Department of Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton, NY 11973

As a promising alternative technology to the present electric energy storage utilizing Li-ion batteries, Na-ion batteries (NIBs) have attracted increasing interest for emerging large-scale applications due to the huge abundance and low cost of sodium [1]. Iron fluoride (FeF₂) is a lithium-conversion cathode capable of accommodating multiple-charge transfer per formula unit, and the comprehensive evolution during its lithiation process has been experimentally examined [2, 3]. It is of great importance to verify whether FeF₂ can be adapted to NIBs as well as to understand the underlying electrochemical mechanism of the sodiation reactions.

In this work, we present the first real-time observation of sodiation in FeF₂ nanoparticle (NP) electrode for NIB using the state-of-the-art *in-situ* scanning/transmission electron microscopy (S/TEM) and spectroscopy techniques. The FeF₂ NPs were synthesized by a solution process [4] and then assembled into an in-situ electrochemical cell with amorphous carbon film as both conductive support and charge-transport media (Fig. 1a). All the in-situ measurements were implemented in a Nanofactory holder and performed on a 200-kV JEOL 2100F TEM; the supplementary ex-situ characterization was conducted on an aberration-corrected 200-kV Hitachi HD2700C STEM.

The morphological, structural, and chemical evolutions during sodiation were *in-situ* tracked and recorded, as shown in Figs. 1b – 1e. Upon sodiation, numerous 1-4nm Fe nanocrystallites precipitated within the FeF₂ NPs and gradually populated the entire particle, forming an interconnected network and generating ~30% lateral expansion (Fig. 1b). The crystal structures of pristine and sodiated samples (Fig. 1c) were determined by high-resolution high-angle annular dark-field (HAADF) imaging, and we found a novel sodium hexafluoroferrate (Na₃FeF₆) phase, which has only been theoretically predicted and yet been observed experimentally. This ternary Na-Fe-F phase was further verified using *in-situ* electron diffraction in a parallel way. In addition, by comparing electron energy-loss spectroscopy (EELS) before and after sodiation (Fig. 1d), accommodation of Na and reduction of Fe were consistently confirmed. The EELS elemental mapping (Fig. 1e) also identifies the spatial distribution of ionic sodium and metallic iron. With these consistent and robust findings, we justify the sodiation process via a disproportionation reaction, i.e. $\text{FeF}_2 + \text{Na} \rightarrow \frac{1}{3} \text{Na}_3\text{FeF}_6 + \frac{2}{3} \text{Fe}$. In summary, the methodology and scientific insights obtained in this study are valuable to understanding the generic reaction mechanisms on the atomic scale for both Li- and Na-ion technologies [5].

References:

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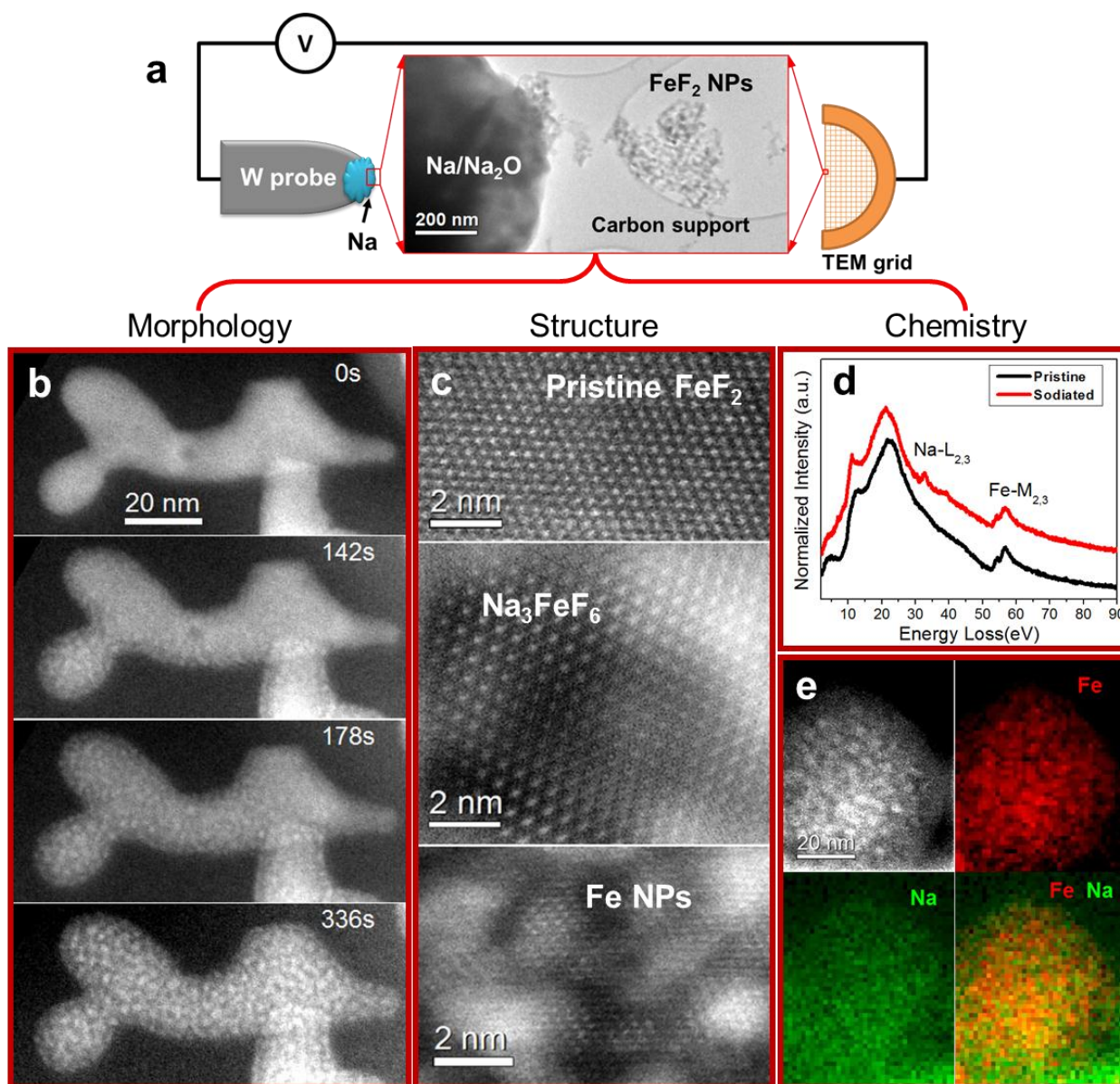


Figure 1. (a) Schematics of in-situ cell setup, with a TEM image showing FeF₂-C composite electrode in contact to Na metal on surface of a piezo-driven W probe in a Nanofactory holder. (b) ADF-STEM images showing the morphological evolution of FeF₂ NPs during sodiation. (c) Atomic-resolution STEM images of pristine FeF₂ and produced Na₃FeF₆ and Fe NPs. (d) EELS spectra from samples before and after sodiation. (e) EELS elemental mapping of Fe (red) and Na (green) in a sodiated NP.