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Journal:	*ChemComm*
Manuscript ID	CC-COM-01-2025-000450.R1
Article Type:	Communication

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COMMUNICATION

In Situ Mössbauer Spectroscopy Confirms Fluoroethylene Carbonate Stabilizes Fe^{4+} in Charged $NaFeO_2$

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Development of Fe-based materials for energy storage are hindered by difficutilies to understand of Fe-ions redox. Here we demonstrate *in situ* Mössbauer spectroscopy to monitor dynamics Fe^{4+} in charged $NaFeO_2$ without dissembling the cell. This allows direct confirmation that a fluoroethylene carbonate (FEC) additive stabilizes the otherwise fast degrading Fe^{4+}.

The adoption of renewable electricity in carbon-free transportation, power grids, and smart manufacturing requires advanced storage cells to bridge the unbalancing gaps between electricity production and consumption.[1] Techno-economic analysis on the needs of these cells consistently highlights the importance of reducing costs while enhancing safety compared to Li-ion cells, [2, 3] which stimulated extensive efforts on developing advanced materials and cell systems.[4] Among these, Fe-based materials have garnered significant attention due to iron's abundance as well as its environmental friendliness and non-toxic nature.[5, 6] However, most Fe-based electrode materials, such as the widely used $LiFePO_4$ cathode, operate on the $Fe^{2+}/^{3+}$ redox couple, which typically exhibits lower electrochemical potentials than other transition metal redox systems, resulting in lower energy densities.[7, 8]

Unlocking the reversible operation of the higher-potential Fe^{3+}/Fe^{4+} redox couple holds significant promises for high energy density cells.[9] However, this remains a substantial challenge as Fe^{4+} is highly reactive—a limitation exemplified by the poor performance of the model compound $NaFeO_2$ cathode in sodium cells [10, 11] While the electrochemical generation of Fe^{4+} during charging is well-documented, experimentally observed concentrations of Fe^{4+} are typically limited to around 20%, and accompanied by rapid degradation.[12] This degradation is hypothesized to stem from spontaneous chemical reactions and/or migration of Fe^{4+} to less electrochemically active sites .[13] Consequently, $NaFeO_2$ suffers from low Columbic efficiency, increasing voltage hysteresis, rapid cycling degradation, and pronounced self-discharge.[14] These shortcomings discouraged exploration of $NaFeO_2$ and its related compounds in practical cells despite their cost and energy density advantages.[15] Recent advancements in electrolyte chemistry, particularly the incorporation of fluorinated solvent additives, have demonstrated improved cycling stability for $NaFeO_2$; however, the underlying mechanisms behind these improvements remain unclear.[16]

Unlike commonly employed X-ray absorption techniques that harness interaction of analyte's electrons with X-rays, ^{57}Fe Mössbauer spectroscopy uses recoil-free nuclear gamma-ray absorption and provide much more detailed information about the local chemical environment of Fe but its applications in *in situ* and operando analysis have been rare due to a number of challenges.[17] In this report we outline our efforts via in situ Mössbauer spectroscopy to visualize formation and degradation of Fe^{4+} in the $NaFeO_2$ cathode. We confirm Fe^{4+} in this cathode experiences at least 20% degradation within 24 hrs even in relatively low state of charge (SOC) conditions. Such degradation was almost eliminated by the application of 5% FEC additive with both the $NaPF_6$ and $NaClO_4$ based electrolyte. On the other hand, although Fe^{4+} disappearance was generally observed in the absence of FEC, no Fe-based side products such as iron oxides were observed during degradation.

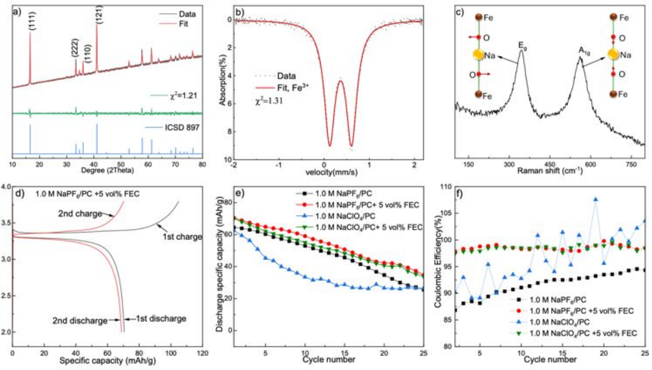

Figure 1: characterization of O3-$NaFeO_2$ cathode employed in this work: a) X-ray diffraction patten and the Rietveld refinement results; b) Mössbauer spectrum; c) Raman spectrum;

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Supplementary Information available: See DOI: 10.1039/x0xx00000x

d) Voltage profiles for the initial two charge-discharge cycles in 1.0M $NaPF_6$/PC with 5% FEC additive; comparison of e) discharge specific capacity and f) Coulombic efficiency of $NaFeO_2$ in the $NaPF_6$/PC and $NaClO_4$/PC electrolytes with and without FEC additive.

Figure 1 presents a set of characterization results of our synthesized $NaFeO_2$ powders that validate the phase purity and electrochemical activity. The X-ray diffraction (XRD) pattern shown in Figure 1a and the extracted lattice parameters using refinement confirms the group R-3m hexagonal layer structure with lattice parameter of a = 3.027 Å and c = 16.104 Å (Rietveld refinement details in Table S1). This structure is characterized by octahedrally coordinated sodium and iron ions, arranged in a repeating layered pattern within a unit cell (Figure S1b).[18] Scanning electron microscopy characterization reveals platelet particle morphology (Figure S1a), while energy-dispersive X-ray spectroscopy (EDS) quantifies the Na to Fe atomic ratio as 1 to 1 (Figure S2). The Mössbauer spectroscopy of pristine $NaFeO_2$ powders show a pure doublet peak with an isomer shift (IS) of 0.364 mm/s and quadrupole splitting (QS) of 0.485 mm/s as expected (Figure 1b).[12, 14] The Raman spectrum also reveals the expected Eg and A1g resonance peaks in accordance with the perpendicular vibration to optic axis and vibration of two adjacent anion layers moving parallel to optic axis, respectively, that both agree with literature (Figure 1c).[19, 20]

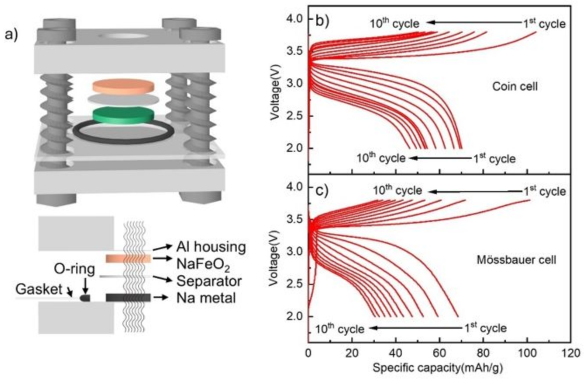

Figure 2: a) schematic illustration of the Mössbauer spectroscopy cell employed in this work and b-c) validation of its function with similar voltage profiles from a standard coin and a Mössbauer cell.

Figure 1d presents the voltage profiles of the $NaFeO_2$ cathode at 10 mA/g in 1.0 M $NaPF_6$ in propylene carbonate (PC) with 5.0 vol% of FEC. The cell exhibited an initial de-sodiation capacity of ~ 100 mAh/g, which corresponds to 0.42 mol of Na removal per mole of $NaFeO_2$, assuming no anionic redox or parasitic electrolyte oxidation reactions. The following discharge capacity was ~70 mAh/g. The capacity gradually decayed over the subsequent cycling. This degradation was commonly attributed to the instability of the Fe^{4+} and/or the de-sodicated layered FeO_6 lattice.[21] In addition to this electrolyte, the FEC-free 1.0 M $NaPF_6$ in PC was also examined along with the $NaClO_4$ in PC electrolyte both with and without the FEC additive. Cycling results from these electrolytes are summarized in Figure 1e-f. The $NaFeO_2$ cathode exhibited electrolyte-dependent Columbic efficiencies and the capacity retentions for 25 cycles were 50% and 40% for the $NaPF_6$/PC electrolyte with and without FEC additive, and 48% and 41% for the $NaClO_4$/PC electrolyte with and without FEC additive, respectively. Therefore, the addition of FEC clearly improves the performance, which matches the literature.[16] Considering that the Fe^{4+}/Fe^{3+} redox is the primary contributor to the capacity, Mössbauer spectroscopy is a promising tool to decipher the mechanism by which FEC improves performance.

To carry out the Mössbauer spectroscopy analysis, homemade in-situ cells were used. These cells were assembled with two pieces of aluminum blocks as shown in Figure 2a. The center of each block was milled with a ½ flat top endmill to a slight thickness of around 0.5mm (optimized based on transmittance of gamma rays and mechanical strength, transmission was ~ 65%, Figure 2). A pre-cut PTFE gasket was used to separate these two blocks from direct electrical contact, while an O-ring (dash number 116) was used to seal cell components. No absorption feature was not observed in absence of the $NaFeO_2$ cathode as expected. The feasibility of this Mössbauer cell was validated with the similarity in voltage profiles and charge-discharge capacity to a standard coin cell (Figure 2b). Although the Mössbauer cell exhibited slightly higher overpotential and lower initial open circuit voltage due to larger cell resistance as spacers and springs standard to coin cells were not used, this outcome does not affect the analysis as the cell function well in terms of representing coin cells on the generating and maintaining Fe^{4+}. A fresh cell was assembled for each testing condition and each condition was repeated in triplicates to ensure consistency.

In a typical Mössbauer measurement, a voltage limited charging protocol is employed to charge the $NaFeO_2$ cathode to a designated state-of charge (SOC) state at 10 mA/g. The acquisition of Mössbauer spectrum starts immediately upon completion of charging and the voltage of the cell was hold constant during Mössbauer measurement (charged state spectra). After completion of this initial spectrum, the cell charging cables were disconnected and the cell was left resting at open circuit (OSV) for 24 hrs. After resting a second spectrum was immediately acquired while keeping the charge cable disconnected (after 24hrs rest spectra). The $NaFeO_2$ mass loading in the Mössbauer cell was optimized as ~ 20 mg/cm^2 based on consideration of matching with standard cells (typically at 1.5 mAh cm^{-2}) and reasonable Mössbauer spectra acquisition duration. Given the natural abundance of ^{57}Fe as 2%, each electrode has 0.2 mg of active ^{57}Fe and this necessitates a 24 hrs duration for each Mössbauer measurement.[22]

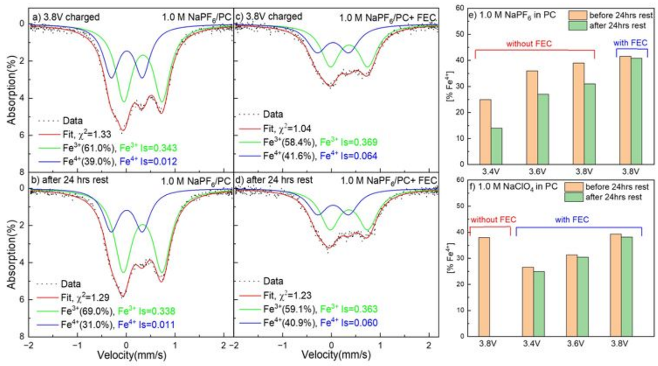

Figure 3: Mössbauer spectra and fitting results of $NaFeO_2$ cathodes charged to 3.8V before (a, c) and after (b, d) 24 hrs resting at open circuit in electrolytes of a,b) $NaPF_6$ in PC; c,d) $NaPF_6$ in PC with FEC additive. The changes in quantified Fe^{4+} population are compared in e) for the $NaPF_6$-based and f) $NaClO_4$ based electrolytes as a function of voltage.

The first Mössbauer spectroscopy analysis was performed with the 1.0 M $NaPF_6$/PC electrolyte. The acquired spectra are presented in Figure 3a-b (for 3.8V) and Figure S3 (for 3.4V and 3.6V) along with the fitting results. The fitting parameters are tabulated in Table S2-3. Notably, all spectra have a doublet component with mirror intensity and an IS value of near 0 mm/s, which corresponds to high spin Fe^{4+} species.[23] The relative population of this Fe^{4+} species is proportional to the charging voltage and reached to ~ 40% in a cathode charged to 3.8V (Figure 3a). This confirmed that the Fe^{4+}/Fe^{3+} redox is primarily responsible for cell charging. Stability of Fe^{4+} was analyzed based on the comparison to the Mössbauer spectra acquired from the same cell but after 24 hrs resting at open circuit. The comparisons reveal at least 20% decays of Fe^{4+} at all voltages examined (3.4, 3.6 and 3.8V), including from the initial 25% to 14% at 3.4V (Figure S3a-b), from 36% to 27% at 3.6V (Figure S3c-d), and from 39% to 31% at 3.8V (Figure 3a-b). The decay in Fe^{4+} concentration was accompanied by an increase in concentration of Fe^{3+} that has same Mössbauer fitting as the Fe^{3+} in pristine $NaFeO_2$. No new Fe^{3+} species were observed with the $NaPF_6$ electrolyte.

The impact of FEC additive on stabilizing Fe^{4+} was then examined with the 1.0M $NaPF_6$/PC electrolyte with 5 vol% FEC additive (Figure 3c-d). The population of Fe^{4+} in cathode charged in this electrolyte at 3.8V was approximately 42%, which is similar to the FEC-free electrolyte (Figure 3c). The stability of Fe^{4+} during resting, however, was significantly improved with FEC as neither reduction in Fe^{4+} concentration or change in Mössbauer parameters was observed after 24 hrs OCV resting (Figure 3d-e), which is an important feature as it provides direct evidence on validating the beneficial role of FEC on stabilizing charged interfaces. It is pivotal because cells are typically stored under charged conditions.

Also analyzed was the formation and stability of Fe^{4+} in 1.0M $NaClO_4$ in PC electrolyte with and without FEC as these electrolytes are also commonly used in Na-ion cells.[24] The acquired Mössbauer spectra are presented in Figures S4-5 with the fitting parameters detailed in Tables S4-5. The changes in relative populations of Fe^{4+} are compared in Figure 3f. The relative concentration of Fe^{4+} when charged in the FEC-added electrolyte at 3.4 V was 27%, which was reduced slightly to 25% after 24 hrs OCV resting (Figure S4). Similarly, at 3.6V the relative concentration of Fe^{4+} decreased from the initial 31% to 30% after OCV resting, and from 39% to 38% in the one charged at 3.8V. In strong contrast, the cathode charged to 3.8V without FEC contained an initial 38% Fe^{4+}. However, such Fe^{4+} disappeared almost entirely during resting and transformed into a high spin Fe^{3+} state as shown in Figure S5. While the exact chemical reactions behind such a dramatic degradation remain unclear, perchlorate salts are known to be highly hygroscopic. These salts, therefore, likely held trace amounts of water, which can readily react with Fe^{4+}.

The clear and strong differences exhibited in Fe^{4+} stability from both $NaPF_6$ and $NaClO_4$ based electrolytes contribute to convincing evidence on the beneficial roles of FEC for stabilizing Fe^{4+}. Fe^{4+} is known to be highly reactive, and its degradation in electrochemical interfaces is presumably coupled with chemical redox reactions with electrolyte. The reduced degradation with FEC suggests FEC fundamentally eliminated such redox reactions, which corroborate well with prior comprehensive cathode-electrolyte interface (CEI) analysis that validates formation of thinner and stronger CEI layers with enriched inorganic components with assistance of FEC.[16] The reduced degradation leads to a more stable and closer to 100% columbic efficiencies, higher and less decaying resting voltage, as well as reduced self-discharging as presented in Figure 1e-f and S6. However, this surface stabilization alone is insufficient in addressing cycling instability of $NaFeO_2$ due to its fundamental structural limitations such as potential migration of Fe to electrochemically inert crystal sites. [14]

Overall, employing $NaFeO_2$ cathode as a model system, we present application of in situ Mössbauer spectroscopy to track dynamic formation and degradation of Fe-species in cells environment. Formation of Fe^{4+} during charging was validated and its dynamic degradation was quantified as at least 20% within 24 hrs resting at OCV in FEC-free electrolytes. The FEC additive effectively eliminate this degradation at least for 24 hours as the concentration of Fe^{4+} and the local chemical environment during resting was unchanged, which lead to improved columbic efficiency and reduced self-discharging. This initiating study is expected to stimulate exploration of Mössbauer spectroscopy for better understanding and control of electrochemical devices. Although it is difficult for this technique to probe transit events due to significantly lengthy data acquisition compared with X-ray based techniques, information from the average of these events still provides critical information for mechanistic understanding such as the ones presented here. The lengthy acquisition can also be significantly reduced if ^{57}Fe isotope enriched samples were employed.

Conflicts of interest

There are no conflicts to declare

Data availability

The data supporting this article have been included as part of the supplementary information.

Acknowledgements

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under award DE-SC0023266. Microscopy and Raman portions of this research were supported by the Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

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Data Availability Statement

The data supporting this article have been included as part of the supplementary information