Supporting Information

Endogenous Dynamic Nuclear Polarization for Sensitivity Enhancement in Solid State NMR of Electrode Materials

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1. X-ray powder diffraction

\[ \text{Figure S1} \] X-ray powder diffraction patterns of the undoped and doped Fe LTO samples compared with the simulated pattern taken from the ICSD.

2. Room temperature $^6$Li NMR measurements

Room temperature $^6$Li NMR measurements were performed in order to determine the Fermi contact shift of Li sites around the Fe dopants. Rotor synchronized Hahn echo sequence was used on samples spinning at 60 kHz. A short recycle delay of 50 ms was chosen in order to give the Li environments in the vicinity of the dopant higher weight in the spectrum. We note that the we expect here that Li sites bonded to Fe (III) through a bridging oxygen are not quenched at room temperature and can therefore be detected even though at 100 K they may be quenched. This expectation is based on two assumptions: (i) The main cause for quenching is fast transverse nuclear relaxation which results in severe broadening. In this case transverse relaxation will be mostly driven by the electron longitudinal relaxation through its modulation of the electron-nuclear couplings. Treating the electron relaxation time, $T_{1e}$, as the correlation time of the motion in the system, when $1/T_{1e}$ is of the order of the nuclear Larmor frequency ($\omega_n=58$ MHz), it will drive
both longitudinal and transverse nuclear relaxation since the spectral density, $J(\omega)$, will have non-negligible contribution at both $J(0)$ and $J(\omega_n)$. As the electron relaxation shortens, due to temperature and electron-electron interactions with increasing Fe doping, its efficiency in driving nuclear relaxation will decrease with decreasing $T_{1e}$, since the spectral density will be broader with lower contribution at $J(0)$ and $J(\omega_n)$. (ii) A second contribution to quenching is spectral broadening due to electron-nuclear through space dipolar interactions. These are averaged with increasing efficiency as the electron relaxation becomes faster. Thus, here again we expect that with increasing dopant concentration and temperature, quenching effects will be significantly reduced and finally eliminated.

These assumptions will be investigated thoroughly and quantitatively in a future study.

The room temperature $^6$Li spectra of Fe00125-10 are plotted in Figure S2. The low Fe content sample displayed only a single sharp resonance corresponding to the majority of Li in the sample which are not in close proximity with the dopant. Due to the low concentration of dopant only a small fraction of Li will be broadened and/or shifted by the Fe(III) electrons and are most likely below the detection limit of this room temperature measurement. As the Fe content increased, a broad spectral component appeared, growing in contribution with Fe content. Taking into account the two assumptions discussed above, we assign this resonance to the Li in close proximity of the dopant, which in the Fe10 sample are the major component in the spectrum. This resonance is centered at 1 ppm and has a width of 36 ppm, suggesting the Fermi contact shift is negligible in this compound.

*Figure S2* $^6$Li MAS spectra of Fe-LTO samples acquired at room temperature at 60 kHz MAS.

*Figure S3* Simulation of $^7$Li MIMS ENDOR for the two possible dopant sites, octahedral (top) and tetrahedral (middle) compared with the experimental spectrum (bottom). The dopant is represented by ping ball, Li in green, Ti in Blue and O in red. The first three closest Li distances were taken into account based on the undoped crystal structure (in brackets is the number of Li ions at this distance).
3. ENDOR Simulations

$^7$Li Mims ENDOR spectra were simulated for the two possible doping sites in the spinel structure (based on the undoped structure). In each site the distances to the first three nearest Li ions was simulated.

4. Quenching, absolute and components enhancement factors

The absolute enhancement factors were obtained by taking into account the increasing loss of signal due to quenching by the Fe dopant at 100 K (Figure S4), the shortening of nuclear relaxation of doped samples compared to undoped sample at room temperature and the gain in sensitivity due to performing the experiments at low temperature. For $^6$Li, due to the long relaxation of the undoped sample at 100 K we were not able to acquire a quantitative measurement. Since for $^7$Li there is no significant quenching effect comparing the undoped and Fe00125 samples, we use the $^6$Li Fe00125 signal as a reference point to estimate quenching with increasing Fe content. Absolute enhancement factors obtained for $^6$,$^7$Li are plotted in Figure S5, in comparison to the enhancement determined from the ratio of signal intensity with and without $\mu$waves.

As mentioned in the main text, with increasing Fe(III) content a second broad component was observed in the spectrum (Figure S6a). The spectra of the various samples were deconvoluted in DMFIT$^3$ and the spectral contribution of the broad and narrow components is plotted in Figures S6b. This analysis shows that the ratio between these two components was maintained in spectra acquired with and without $\mu$waves. This is also reflected by the
similar enhancement factors obtained for the two components as a function of Fe content (Figure S6c).

5. Quantification of the Fe(III) reduction process
To support the assignment of the redox process observed at about 1.8 V on the cathodic scan in the CV experiments performed on Fe doped LTO we calculate the mole of electrons transferred during that process.

The integrated area under this redox peak vs. time is about 50mAs. Thus the total amount of charge passed in the cell during that process:

\[
\frac{0.05 \text{ C}}{96485 \text{ C/mole}} = 5.2 \times 10^{-7} \text{ mole of electrons.}
\]

The active mass of the electrode was 2.75 mg. Neglecting the change in the molecular weight of the LTO with doping (459.083 g/mol) we obtain that for x=0.1 Fe in LTO formula there are \(6 \times 10^{-7} \text{ mole of Fe(III)}\) in the electrode.

Since there is a transfer of approximately one electron per Fe(III) site we assign this process to the reduction of Fe(III) to Fe(II).

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**Figure S6** (a) \(^7\)Li spectra acquired for the different samples revealing increase in a broad resonance with Fe(III) doping. (b) The spectral contribution of the two components obtained by deconvolution. (c) enhancement factors for the broad and narrow spectral components.
6. EPR measurements on cycled CF-electrodes

Figure S7 (a) Q-band EPR spectra of pristine Fe0025 powder (black) and CF-electrodes acquired after one cycle in the voltage range of 0.9-2.5V (red) and 0.9-4.45V with a holding period on lithiation at 4.45V (blue) acquired at 10 K. The red spectrum display two sharp resonances coming from the capillary with no signal detected from Fe in the sample. (b) MIMS ENDOR spectra acquired for the sample cycled in the broad voltage range in comparison with the pristine Fe0025 sample.

7. Sweep profile of cycled samples

The electrochemistry data suggest that not all Fe is oxidized back to Fe(III) even with the extended potential window since the reduction peak is larger than the oxidation one. In that case, either the concentration of Fe(III) within the particles will be lower compared to the concentration prior to cycling or that the sample will become heterogenous, varying in the Fe(III) content. The change in the shape of the DNP sweep profile may be interpreted as a situation where a fraction of the LTO particles is not active in DNP and contribute a constant value across the sweep profile, independent of the magnetic field. This scenario is described schematically in Figure S8. To examine this point, we used the experimental result of the DNP sweep profile obtained for the pristine powder (pink curve in Figure S8) and calculated the needed contribution of non-active LTO (with a constant signal intensity across the sweep) in order to reproduce the shape obtained in the sweep profile of the cycler Fe-LTO. We found that with about 25% non-active LTO (blue curve in Figure S8) we can reproduce the experimental result for the sweep fairly well (comparing the dark purple calculated curve with the experimental curve in light purple, Figure S8).
Figure S8 Left: Illustration of MIDNP enhancement in part of the LTO particles (highlighted in pink) in which the Fe was reversibly oxidized to Fe(III). Right: Illustration of the effect of heterogenous sample on the DNP sweep profile. The pink and light purple curves are the experimental sweep profiles obtained for the pristine and cycled Fe-LTO samples, respectively. The blue line corresponds to the unreacted fraction of Fe-LTO in the sample which does not contain Fe(III). The dark purple curve is obtained by the sum of the pink and blue curve with weighting factor to match the experimental light purple curve.

References

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