

Supplementary Information

As mentioned in the paper more cells have been tested showing similar results (see **Figs. A1** and **A2**). For all samples, irrespective of the composition, after relaxation the voltage is near or below 4V as can also be seen in **Figs. A1** and **A2**. The polarisation of $\text{Li}_{2.0}\text{FeSiO}_4$ is higher than that of $\text{Li}_{2.2}\text{Fe}_{0.9}\text{SiO}_4$, but a clear explanation of that has not been found. Nevertheless, the polarisation of $\text{Li}_{2.2}\text{Fe}_{0.9}\text{SiO}_4$ is similar to that observed by Deng *et al.*¹⁻³. They also reported a reduction in the polarisation upon doping with Zn^{2+} , Cu^{2+} or Ni^{2+} .¹ Clearly in our case we can see $\text{Li}_{2.2}\text{Fe}_{0.9}\text{SiO}_4$ as a lithium doped $\text{Li}_{2.0}\text{FeSiO}_4$ as we replaced iron for lithium. It is further stressed that once the cell has been charged up to 4.8V, the polarisation has been increased. This may be a result of the parasitic reaction of the silicate with the electrolyte, possibly induced by the initial formation of Fe^{4+} , which instantaneously react with the electrolyte, forming a Solid Electrolyte Interphase (SEI). This SEI then increases the impedance of the cell and hence the polarisation.

Despite the polarisation, the calculated Li content in the structure has not been influenced by that, as polarisation in itself doesn't consume electrons. Only in the case the cell has been charged beyond 4V, case was taken so as to compensate for the parasitic reactions as mentioned in the text.

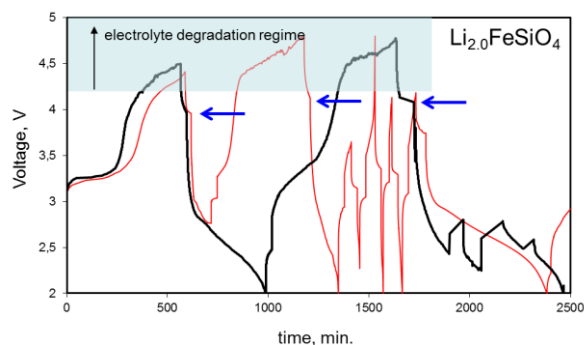


Figure A1. Electrochemical measurement of two cells containing $\text{Li}_{2.0}\text{FeSiO}_4$ showing similar results. The blue arrows indicate the relaxation potentials, which are always near or below 4V. The charge/discharge profile in red showed various in-between charges and discharges.

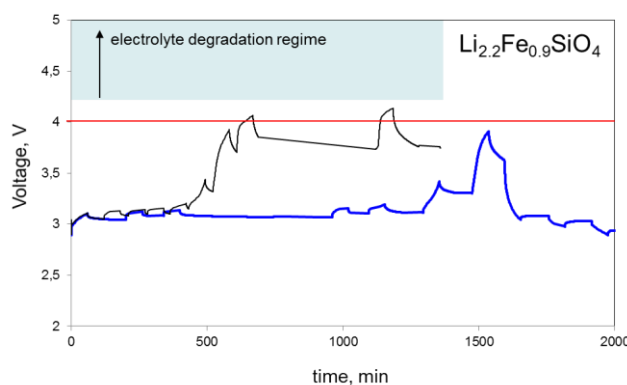


Figure A2. Electrochemical measurement of two cells containing $\text{Li}_{2.2}\text{Fe}_{0.9}\text{SiO}_4$ showing similar results. The red line indicates the 4V limit.

References

1. C. Deng, S. Zhang, S.Y. Yang, B.L. Fu, L. Ma, *J. Power Sources*, 2012, **196**, 386
2. C. Deng, S. Zhang, B.L. Fu, S.Y. Yang, L. Ma, *Mat. Chem. Phys.*, 2010, **120**, 14
3. C. Deng, S. Zhang, G.S. Zhao, Z. Dong, Y. Shang, Y.X. Wu, and B.D. Zhao, *J. Electrochem. Soc.*, 2013, **160**, A1457