

Supporting Information for

**‘Elucidating the origins of path hysteresis during electrochemical cycling of Li-Sb electrodes’**

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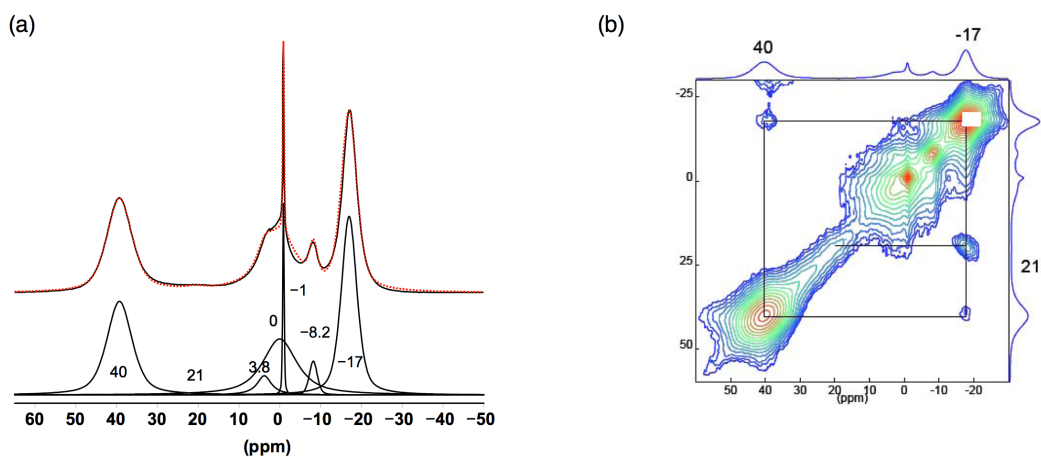


Figure S1: (a)  $^7\text{Li}$  MAS NMR spectrum and deconvolution and (b) two-dimensional  $^7\text{Li}$  exchange NMR spectrum obtained for  $\text{Li}_{1.5}\text{Sb}$  (stopped after 15 hours of discharge), using a mixing time of 10 ms. Spectra were acquired using a MAS rate of 30 kHz.

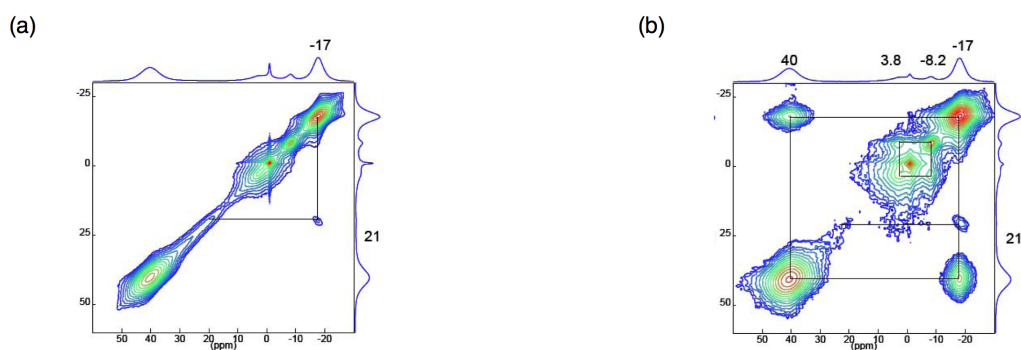


Figure S2: Two-dimensional  $^7\text{Li}$  exchange NMR spectra for  $\text{Li}_{1.5}\text{Sb}$  (stopped after 15 hours of discharge) obtained using mixing times of (a) 0.1 ms and (b) 200 ms. Spectra were acquired using a MAS rate of 30 kHz.

The  ${}^7\text{Li}$  and  ${}^6\text{Li}$  MAS NMR spectra obtained for  $\text{Li}_{2.25}\text{Sb}$  are shown below with the corresponding deconvolutions. Initially the  ${}^7\text{Li}$  NMR spectrum was fitted using the resonances described in the main text. However, it was discovered that an additional resonance was present at 7 ppm. Two-dimensional  ${}^6\text{Li}$  exchange experiments, completed using a mixing time of 50 ms, indicate cross-peaks among the resonances at 7, 3.5 and  $-6$  ppm, suggesting the small resonance at 7 ppm belongs to  $\text{Li}_3\text{Sb}$ . Deconvolution of the  ${}^7\text{Li}$  NMR spectra obtained for further lithiated samples (not shown here) all confirm the existence of the resonance at 7 ppm, suggesting it corresponds to a Li defect site in  $\text{Li}_3\text{Sb}$ .

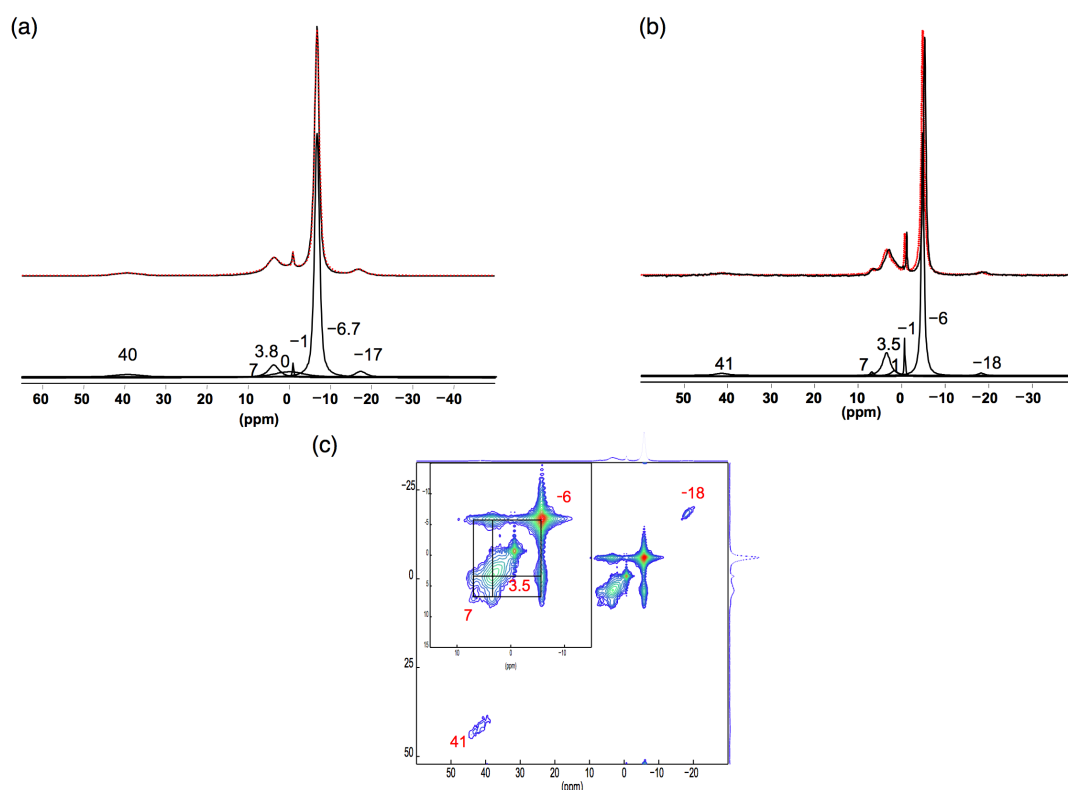


Figure S3: Deconvolution of (a)  ${}^7\text{Li}$  and (b)  ${}^6\text{Li}$  MAS NMR spectra obtained for  $\text{Li}_{2.25}\text{Sb}$  (sample stopped after 22.5 hours of discharge). (c) Two-dimensional  ${}^6\text{Li}$  exchange NMR spectrum for  $\text{Li}_{2.25}\text{Sb}$ , acquired using a mixing time of 50 ms. All spectra were acquired using a MAS rate of 30 kHz.