Understanding the Behavior of LiCoO₂ Cathodes at Extended Potentials in Ionic liquid - Alkyl carbonate Hybrid Electrolytes

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Figure S1. Comparison of LP30 and HE cycled cells after a) 1^{st} cycle and b) 60^{th} cycle in the potential window of 3 - 4.2V vs. Li/Li⁺, TEM images of (c) Li /LP30/ LiCoO₂ and (d) Li /HE/LiCoO₂ after cycling to 4.2 V vs. Li/Li⁺.



Figure S2. Thermal Analysis of delithiated $LiCoO_2$ cycled in LP30, HE and neat [C3mpyr] [TFSI] electrolytes with the potential cut off at 4.2 V vs. Li/Li^+ . (a) Differential Thermal Analysis and (b) Thermogravimetric Analysis



Figure S3. Survey spectrum of delithiated LiCoO₂ electrodes cycled in (a) LP30 and (b) HE.



Figure S4. S 2p XPS spectrum of LiCoO₂

electrode cycled in HE



(b) Rietveld refined fit of the LiCoO₂ structural model to the first *in situ* synchrotron XRD dataset. Data are shown as crosses, the calculated Rietveld model as a line through the data, and the difference between the data and the model as the line below the data. The vertical reflection markers are for LiCoO₂. Some preferred orientation is found in this sample, see reflection $2\theta \sim 20^\circ$, (c) Stacked plot of *in situ* synchrotron XRD data correlated to the potential and corresponding to the lower angle region shown in Fig. 10d. Splitting of the 003 reflection is seen at about 4.57V, (d) Rietveld refined fit of the Li_xCoO₂ structural model to the *in situ* synchrotron XRD dataset at 4.3V. Data are shown as crosses, the calculated Rietveld model as a line through the data, and the difference between the data and the model as the line below the data. The vertical reflection markers are for LiCoO₂. Some preferred orientation is found in this sample, see reflection 20 ~ 20°, (d) Rietveld refined fit of the Li_xCoO₂ structural model to the *in situ* synchrotron XRD dataset at 4.3V. Data are shown as crosses, the calculated Rietveld model as a line through the data, and the difference between the data and the model as the line below the data. The vertical reflection markers are for LiCoO₂. Some preferred orientation

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Figure S6. Plot of ionic conductivity from room temperature to 60°C in hybrid electrolytes



Figure S7. Charge-discharge capacity of HE at 40°C at extended voltage of 4.4V vs. Li/Li⁺.