Interactions of cation disordered rocksalt cathodes with various electrolytes

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Introduction

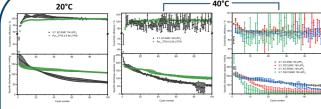
The ongoing development of cathode materials is a key strategy for further increasing the energy density of LIBs.[1] Cation disordered rocksalt cathode materials have gathered increased research interest over the last couple of years due to their high specific capacity and wide array of available element combinations.[2] Up to now, it is still unclear whether the capacity fading observed for this type of material is solely due to the occurrence of not fully reversible anionic redox reactions and consequent material degradation, or also contributed by the side reactions between the cathode material and carbonate-based electrolytes.[3] In order to address it, this study compares the differences in electrochemical performance of a rocksalt Li_{1.25}Fe_{0.5}Nb_{0.25}O₂ cathode, that was shown to involve oxygen redox reaction via a reductive coupling mechanism,[4] and cathode electrolyte interphase (CEI) formation in both lithium metal and lithium ion cells between using a conventional carbonate-based electrolyte and an ionic liquid-based electrolyte.[5]

Experimental

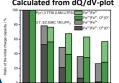
Carbon coated $\mathrm{L}_{1.25}\mathrm{Fe}_{0.3}\mathrm{Nb}_{0.23}\mathrm{O}_2$ as cathode active material Active material P/Vaff/Super C65 80: 10: 10 3-Electrode Swagelock cell (2032 Coin cells and pouch cells for Li-ion set-up) Electrolyte 150 μ L (50 μ L for coin cells; 350 μ L for pouch cells) 1 M LiPF $_6$ in 3:7 EC:EMC or 0.5 M LiTFSI in Pyr_{1.3}TFSI electrolyte

Whatman GF/D (1 layer Freudenberg 2226)

Electrochemical performance



Calculated from dQ/dV-plot



- Fast capacity fading previously ascribed solely to material degradation
- Use of IL-based electrolyte leads to higher capacity retention
- CE reaches values above 100% which hints to parasitic reactions Problems are aggravated at elevated temperatures and with the
- use of FEC
- Fading is linked to oxygen redox activity

Gas Evolution

- Volume and composition of the gas phase was investigated using the Archimedean principle and GC-BID
- Substantial ongoing gas evolution with carbonatebased electrolyte
- H₃ and CO evolution can be linked to the oxidation of EC Gas evolution can be a safety hazard

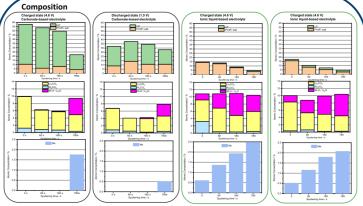
due to rupture of the cell Conclusion

- Carbonate-based electrolytes are not
- ideal for the use with DRX materials An unstable CEI consisting of LiF. Li₂CO₃ and other carbonaceous compounds is detached and re-
- Ionic liquid-based electrolytes can alleviate these

carbonaceous products

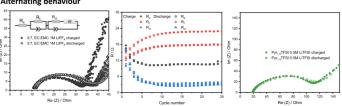
decomposition

CEI Investigation



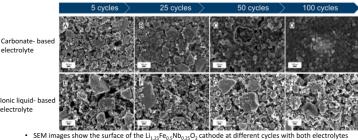
- Composition of the CEI layer was investigated by XPS in the charged and discharged state
- LiF and $\mathrm{Li_2CO_3}$ are main components of the CEI
- Thicker layer covers the cathode surface when carbonate-based electrolytes are used compared to ILs
- Different composition in the charged and discharged state

Alternating behaviour



- Impedance of Li_{1.25}Fe_{0.5}Nb_{0.25}O₂|Li cells were investigated by EIS
- For carbonate-based electrolytes, the resistance of the surface layer $R_{\rm f}$ increases and decreases
- depending on the SOC; R, and R, are independent

Ongoing electrolyte decomposition



- formed during charge and discharge
- problems but further work has to be done for their low ionic conductivity and compatibility with a graphite

- With the carbonate-based electrolyte, the surface is more and more clogged with decomposition
- Electrode pores completely covered after 100 cycles No such behavior with ionic liquids

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