Electrolyte additive investigations: Silicon thin film vs. slurry based composite electrodes
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Motivation and theoretical background
Silicon (Si) is a promising candidate to increase the energy density of lithium-ion batteries. However, silicon suffers from fundamental challenges of high volume changes during cycling which leads to particle breaking and an unstable solid electrolyte interphase (SEI).

We present a comparative electrochemical study of several Si stabilizing electrolyte additives on silicon thin film and slurry based silicon composite electrodes, the latter additionally in full cells. SEI formulation on both electrode types is also studied by X-ray photoelectron spectroscopy (XPS).

Methods and processes
Materials - electrodes and additives
- Silicon thin films by CVD (3 x 30 nm) - 70 µm²/cm²
- Composite electrodes comprising silicon active material, carbon additives and CMC/SBR binder (l + 1 g) - 3 mm²/cm²

- Qs,0 = 3579 mAh/g
- Base electrolyte (1M LiPF6 in EC/EMC/DEC)
- Tested additives:
  - FEC (Fluoroethylene carbonate)
  - SA (Styrene-acrylonitrile)
  - TMMS (Trimethoxymethylsilane)
  - TPFPB (1,1,1-Trifluoro-2,3-difluoro-2-propanol)
  - VC (Vinylenecarbonate)

Electrochemistry
- CV cycles 5 x 1.5 V vs Li/Li+ with a scan rate of 0.1 V/s
- Full cell vs. NCM positive electrode (2.5 V - 4.3 V)
- Galvanostatic cycling @ C/3, one formation step @ C/10, no constant voltage steps

XPS
- PHI Quantera SXM
- C-C bonding referenced to 284.8 eV

Further discussion
- Reason for capacity loss within first 20 cycles (Fig. 3/4)?
- What is the reason for capacity recovery at cycle 40, when using VC (Fig. 3)?
- When using FEC in composite electrodes, the bumps in Fig. 4 most likely indicate FEC depletion. What is the reason for the subsequent temporary recovery?

Additive effects on silicon thin films

Fig. 1: In contrast to reference [1] TMMS does not improve cyclability. Literature results cannot necessarily be adapted to every system. Comparative study of literature proposed additives required.

Fig. 2: Additives enhance cycle life. FEC and VC show similar results. TPFPB and SA show faster capacity fade than FEC.

Fig. 3: FEC stabilizes at 1000 mAh/g until cycle 50, followed by fading with slope comparable to base electrolyte. VC fades until cycle 40 with subsequent recovery. SA and TPFPB show a cycle life worsening effect.

Additive effects on silicon composite electrodes

Fig. 4: Higher additive concentration results in an increased cyclability in case of FEC, not true for VC. FEC is used in every cycle to mend the SEI. Continuous FEC consumption until FEC depletion, indicated by bump in graph. Amount of FEC limits cycle life in half cells.

Fig. 5: FEC improves cyclability also in full cells. However, continuous fading due to lithium (Li) loss by FEC decomposition in every cycle. Cycle stability in full cells may be limited by Li source and not by FEC amount.

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