

Tailored electrolyte design to unlock energy densities competitive with LFP in layered oxide sodium-ion batteries

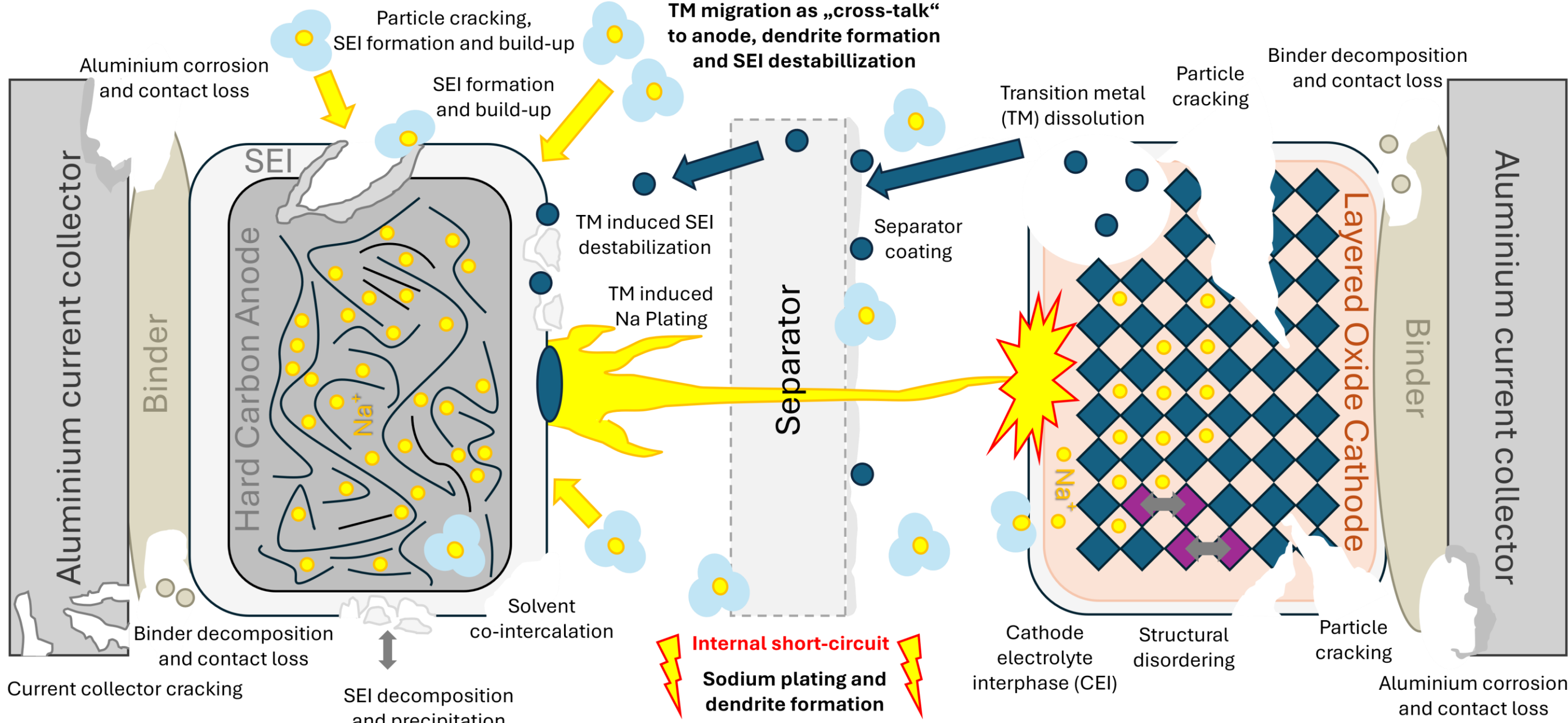


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Electrolyte interphase engineering for SIBs

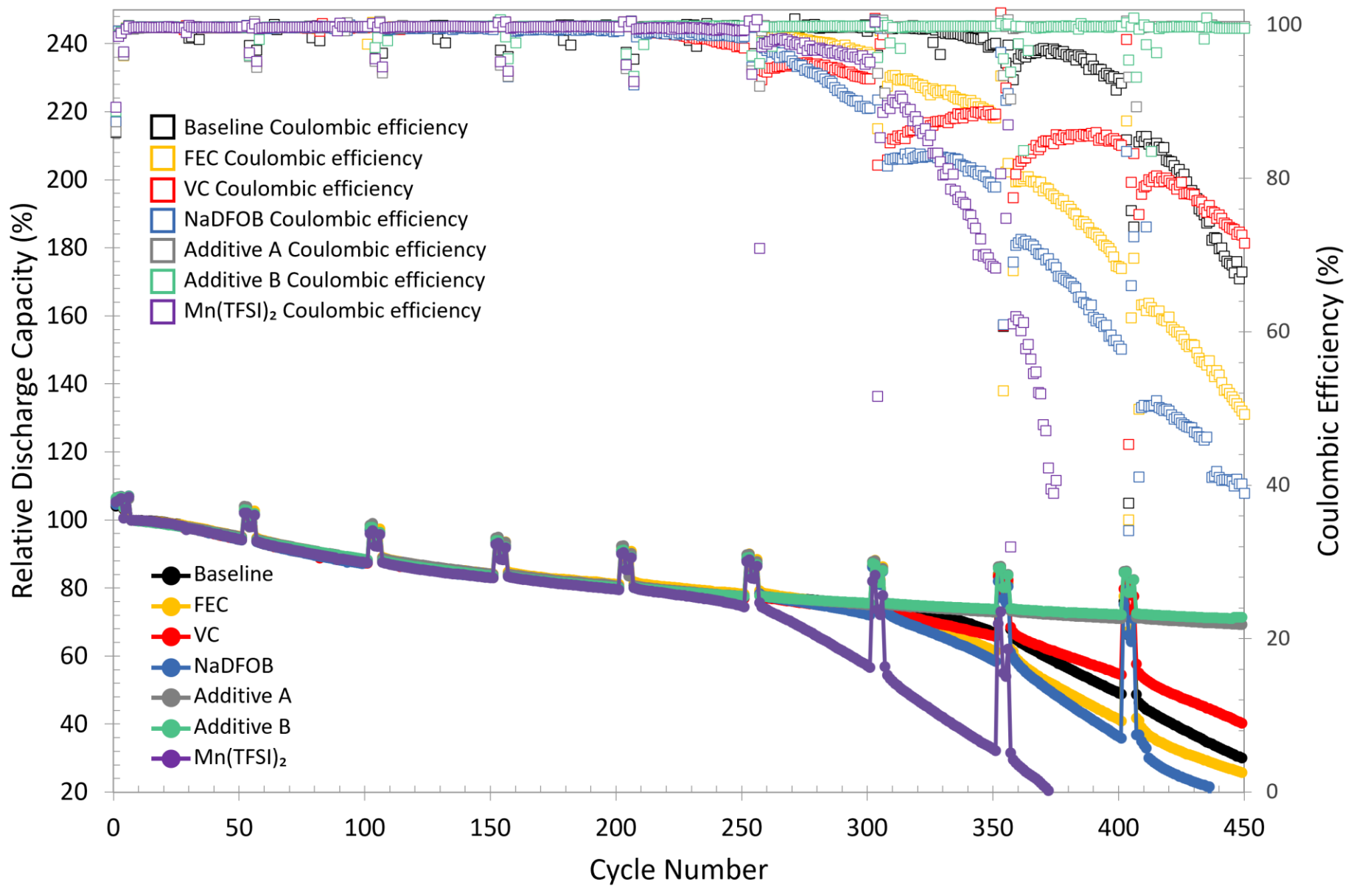
O3-type NFM layered oxides exhibit comparable theoretical specific capacities (~ 160 mAh/g) to LFP (~ 170 mAh/g). To access these comparable capacities, cycling at high cut-off voltages (COVs) > 3.8 V is necessary, although this is widely reported to promote sodium plating on the anode.^[1,2,3] While transition metal (TM), particularly Mn, dissolution and subsequent cross-talk are well-established and investigated failure mechanisms in LIBs^[4], their role in layered oxide SIBs remains insufficiently understood. Therefore, tailored electrolyte interphase engineering is needed to mitigate active material degradation^[1], gas evolution^[2], TM cross-talk and sodium plating^[3]. A set of analytical techniques including electrochemical analyses, SEM/EDX, ToF-SIMS, XPS, ICP-OES and XANES are employed to elucidate the underlying mechanisms and overcoming of TM-induced degradation and sodium plating at high COVs.



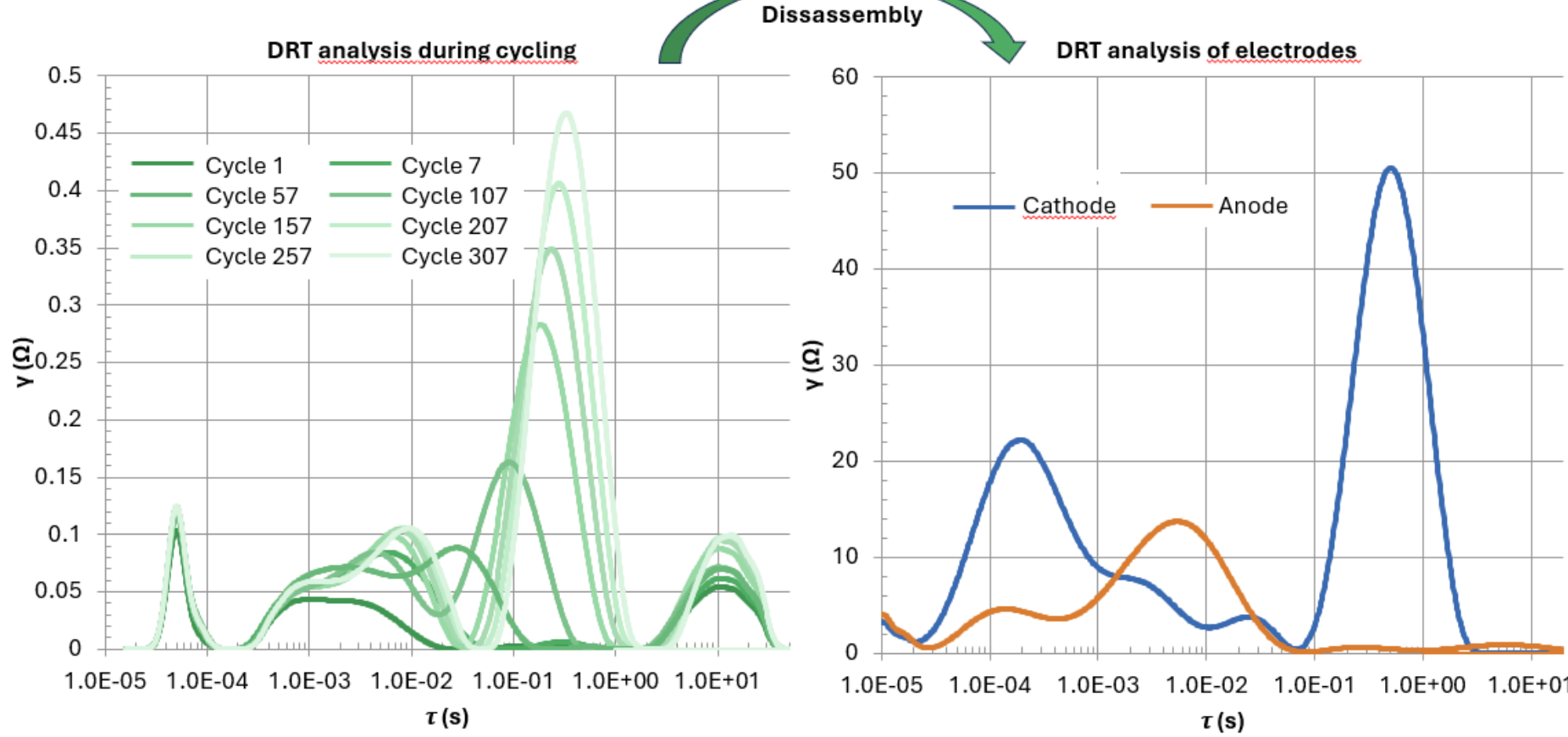
Materials & Methods

- 3 cells per electrolyte of multi-layer wound pouch cell (200 mAh nominal capacity, 200 kPa cell stack pressure, electrolyte amount of 1 mL (~ 5.4 g/Ah)).
- **Baseline electrolyte** is 1.2 M NaFSI in EC:DEC (3:7, by wt.).
- **Na_{0.96}Ca_{0.04}[Ni_{0.24}Fe_{0.30}Mn_{0.37}Zn_{0.09}]O₂** (NFM334-type) as the positive electrode (2% PVDF, 3% carbon black, loading 2.2 mAh/cm²).
- **Hard carbon** as negative electrode (5% PVDF, loading 2.7 mAh/cm²).
- Test plan: CCCV at 1C (200 mA), 40   C, 1.5 – 4.0 V, formation at C/10, two check-up cycles at C/10 and C/3, complemented with a pulse-power test for measuring the DCIR repeating every 50 cycles (Reference-Performance-Test).

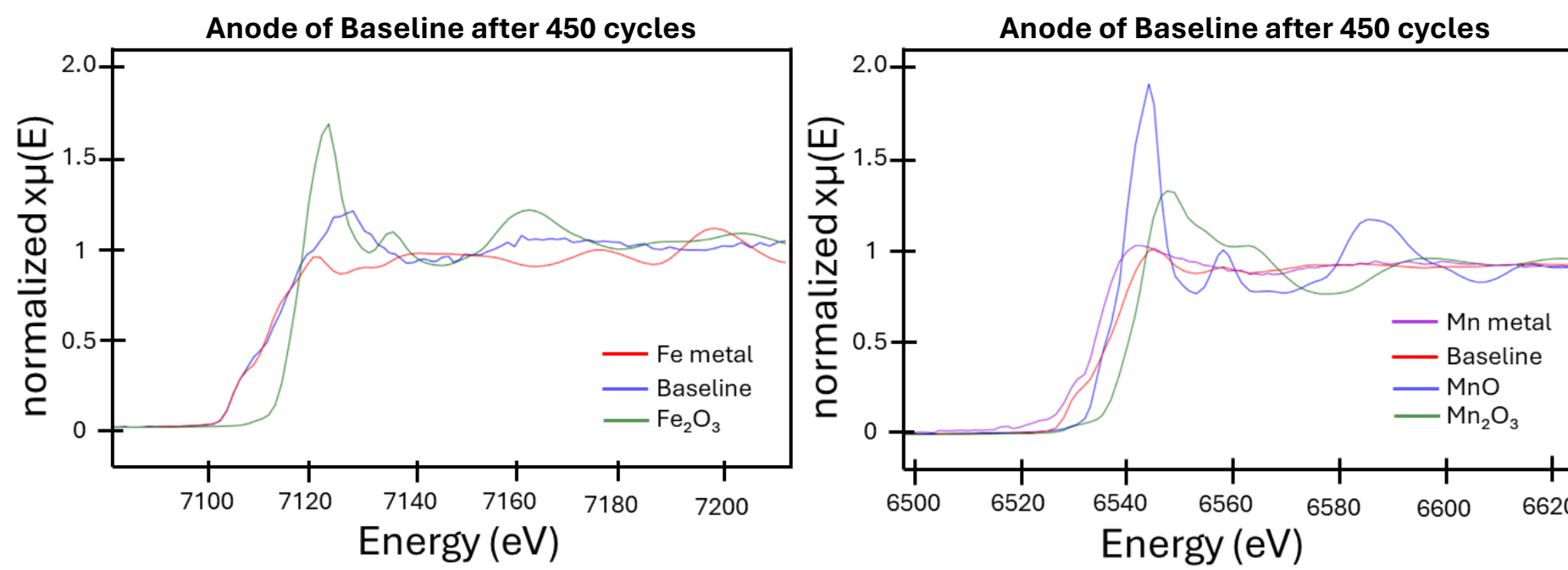
Electrochemical analyses



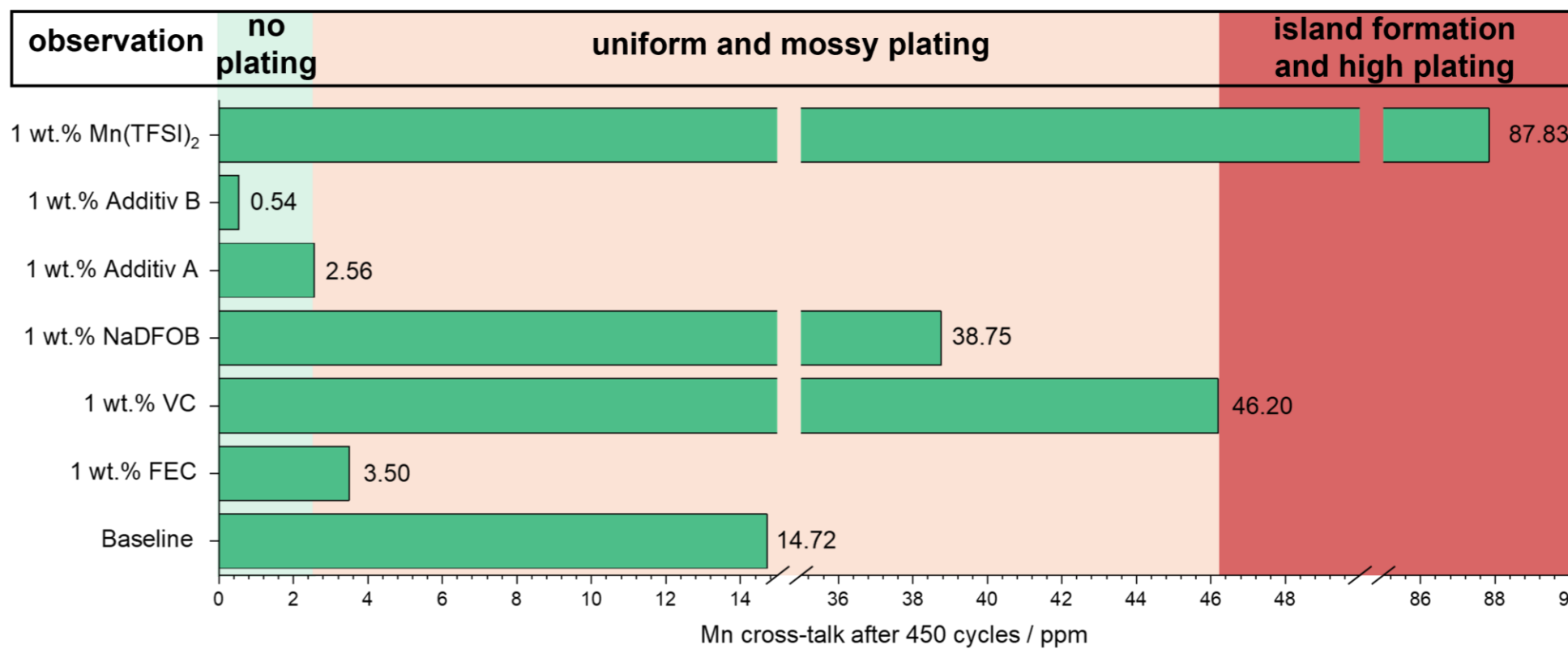
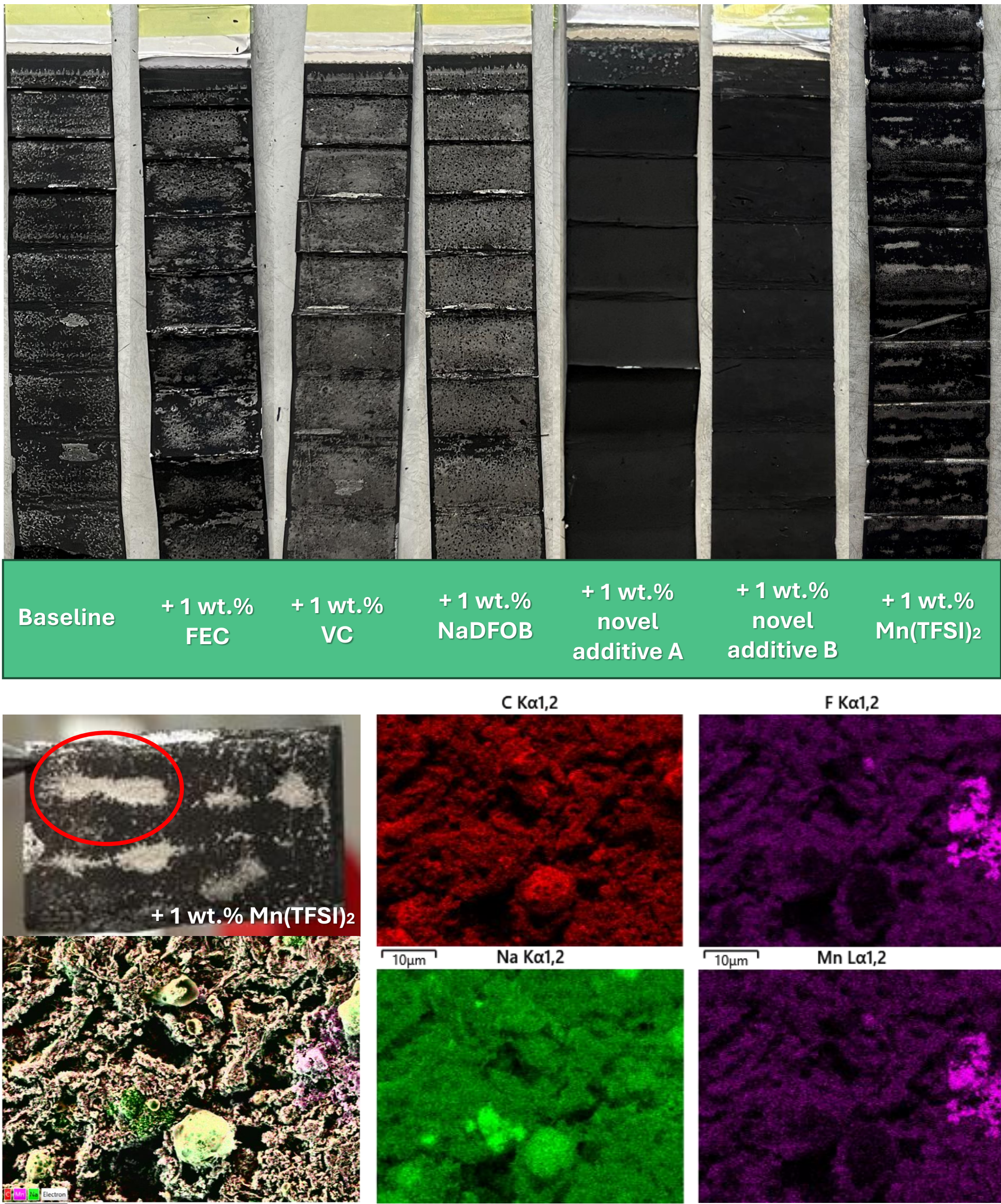
EIS & DRT analysis: Baseline electrolyte



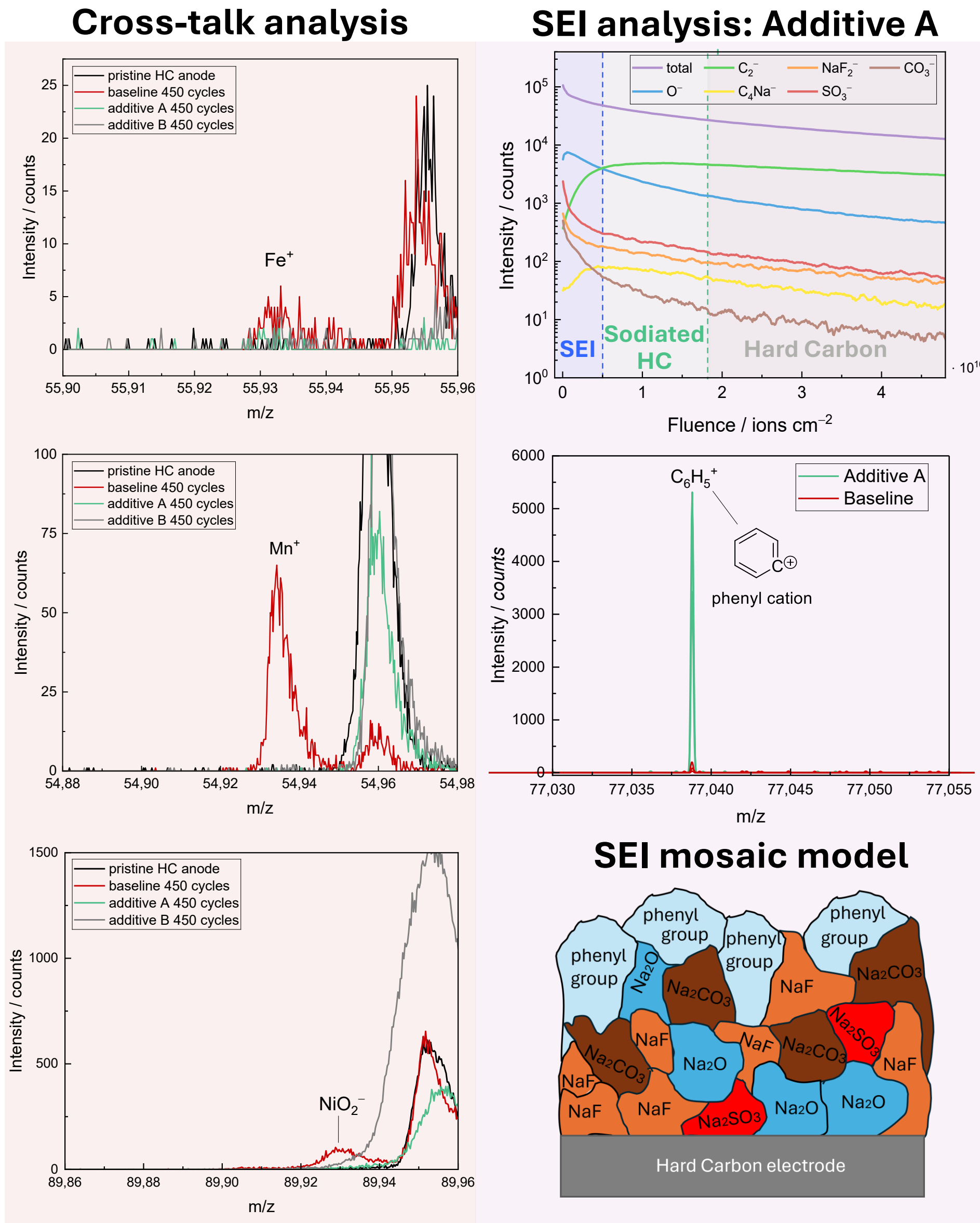
XANES



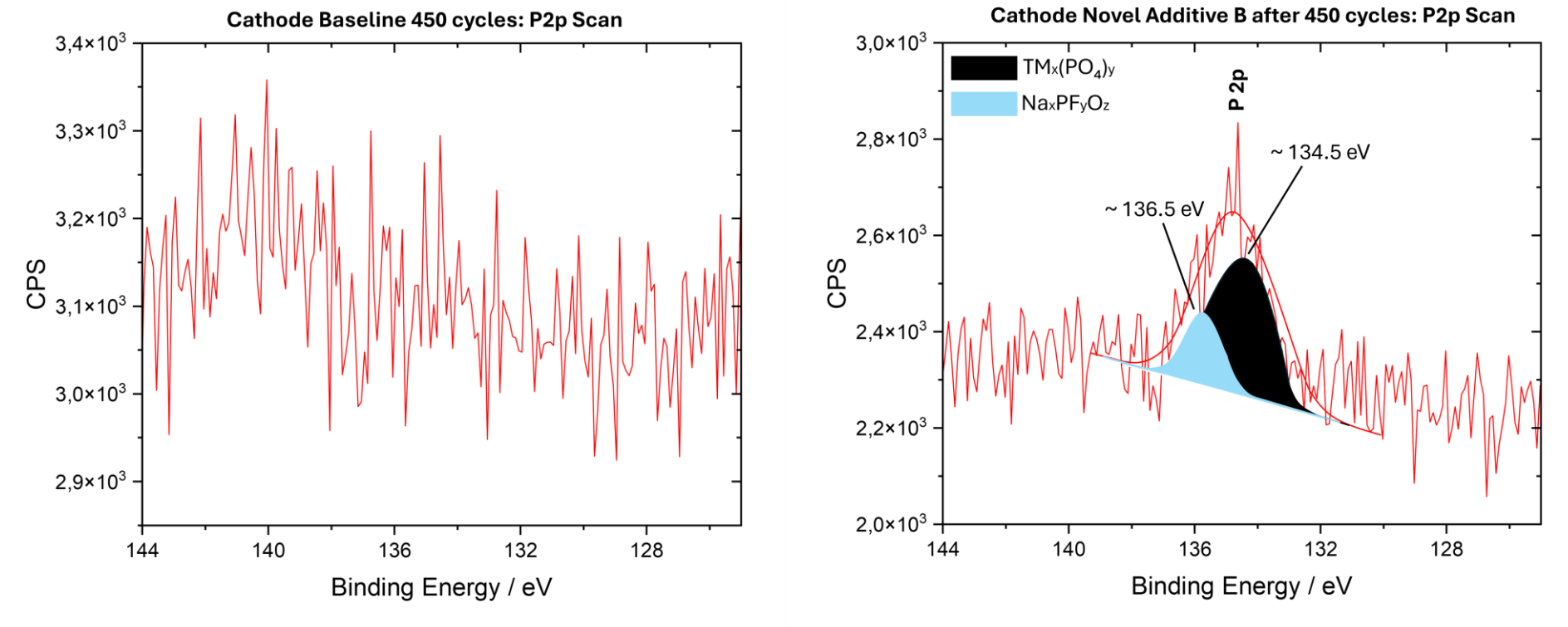
Post-mortem, SEM/EDX & ICP-OES



ToF-SIMS



XPS



Discussion

Various electrolyte additives were screened. Only cells with the additives A & B showed a significant increase in cycle life after 450 cycles while operating above 70% SOH at 4.0 V. A critical point is reached after 250 cycles, where a decline in Coulombic efficiency and an exponential increase in DCIR was observed. DRT analyses link this resistance increase to cathode-related ageing processes.

All TMs from the cathode, but especially different valent Mn species, were detected on the anode after 450 cycles by ToF-SIMS. XANES measurements revealed that Mn and Fe were mostly plated in elemental and mixed valent oxidation states, while Ni and Zn were plated only +II. As confirmed by ICP-OES and SEM/EDX measurements, the size and morphology of the sodium depositions correlate

with the Mn amount, indicating Mn cross-talk as root cause for sodium plating and cell failure. While additive A was identified by ToF-SIMS as SEI builder to protect the anode from TM depositions, additive B presented effective TM-scavenging properties. Further research on effective electrolyte additives for interphase engineering is therefore crucial for operating SIBs at high COVs.

Acknowledgement

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[3] Hijazi, H., Ye, Z., Zhang, L., Deshmukh, J., Johnson, M. B., Dahn, J. R., Metzger, M., J. Electrochem. Soc., 2023, 170, 70512.
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