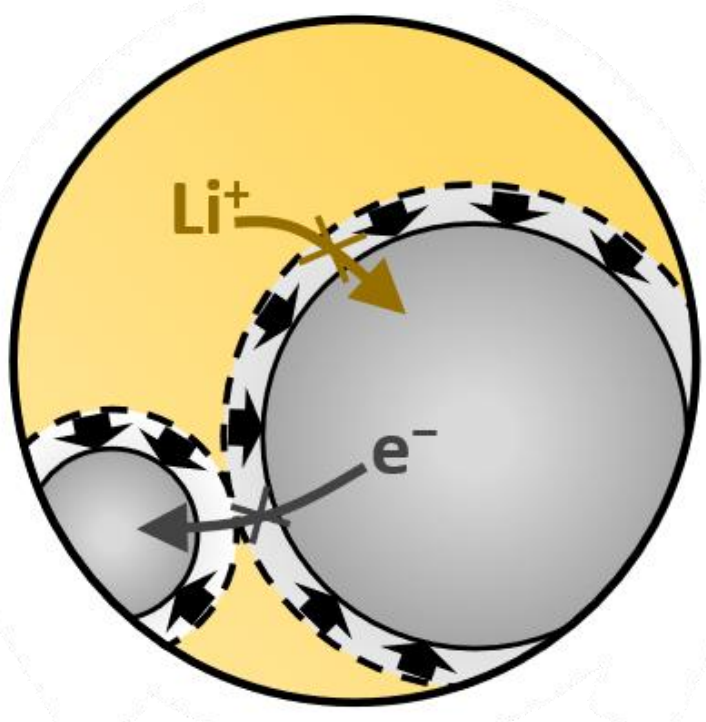


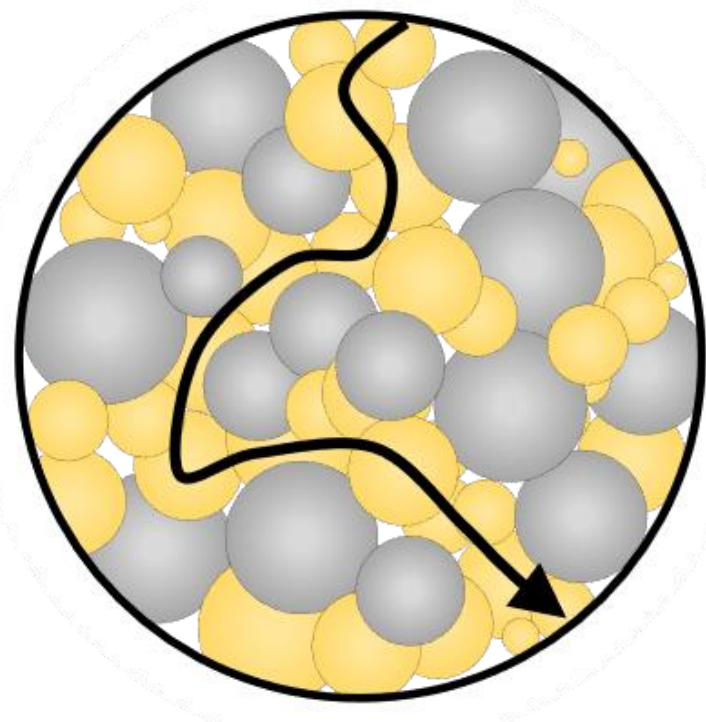


Main challenges in composite cathodes

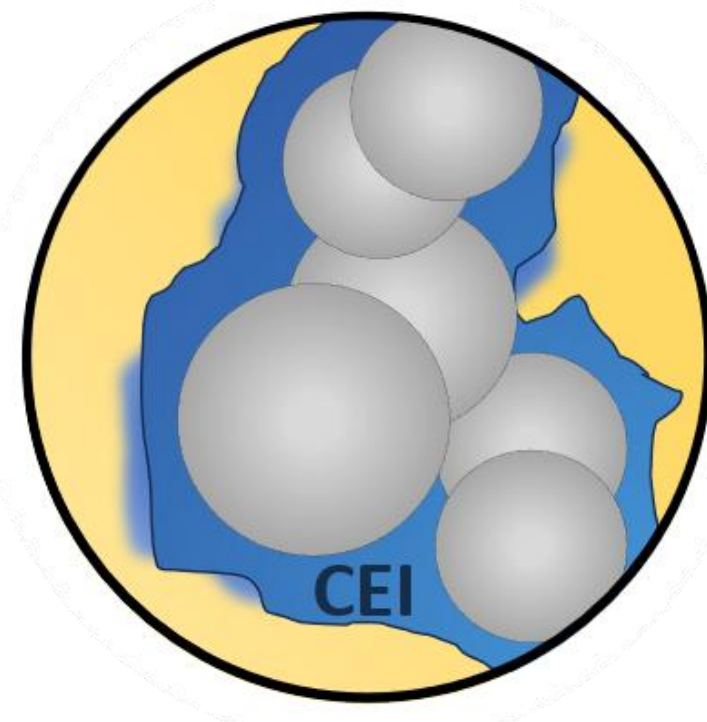
Contact loss



Transport limitations



Interfacial instability

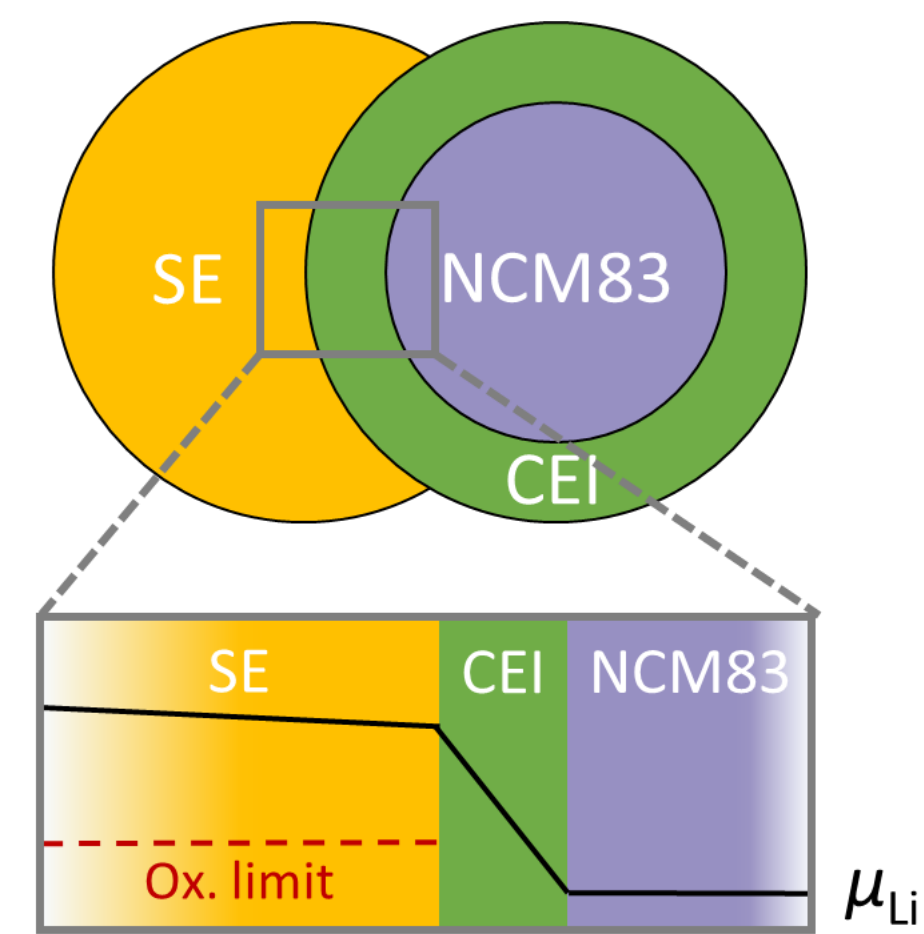


The main challenges include (1) **contact loss** due to changes in active material volume during (de)lithiation, (2) **transport limitations** due to tortuous lithium-ion transport pathways, and (3) **interfacial instability** at the solid electrolyte and cathode active material interface due to electrochemical instability or chemical instability.

Cathode electrolyte interphase (CEI)

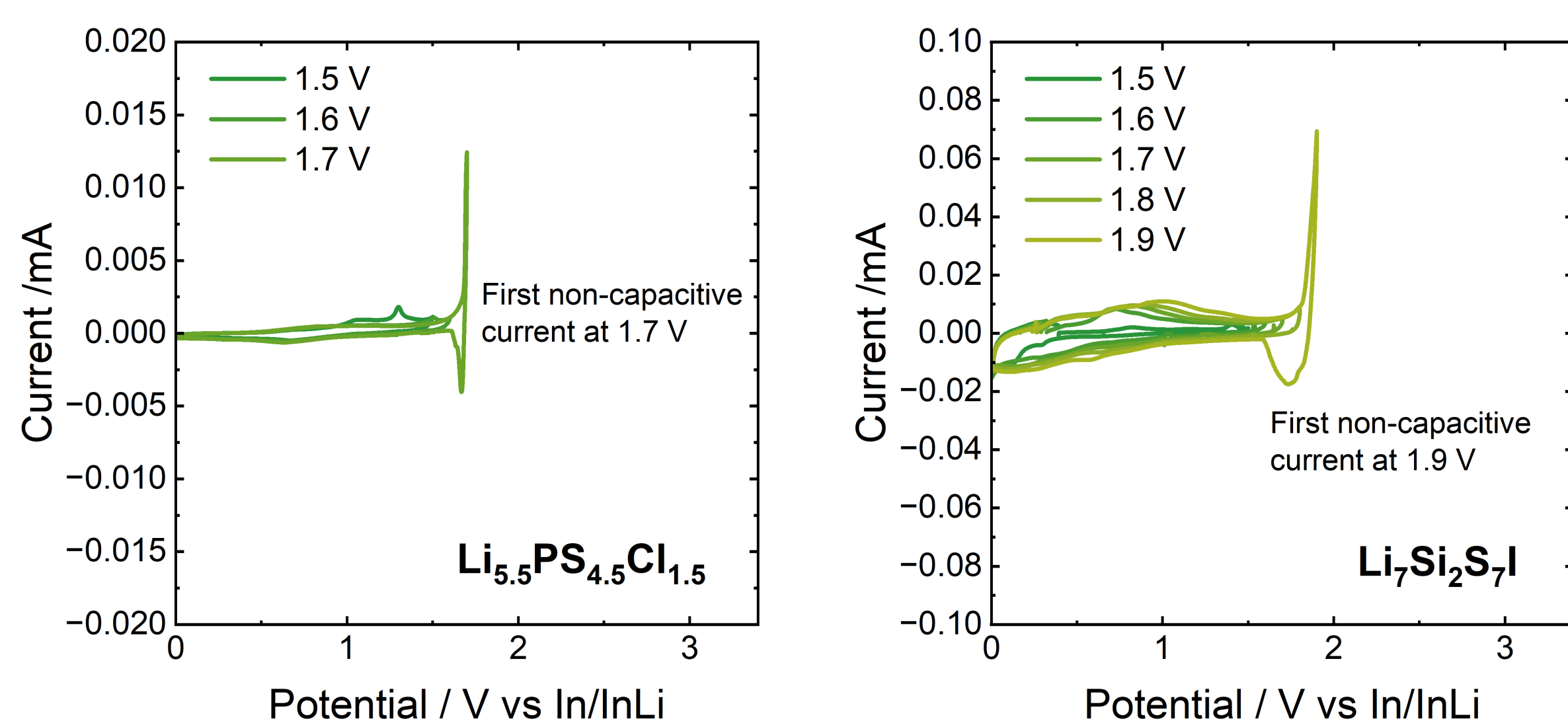
In SSBs using sulfide-based catholytes and NCM as cathode active material, **oxidative decomposition** occurs during charging of the cell.

This is the major contributor to growing cell resistances and thereby leads to **continuous capacity** fading. Finding new solid electrolytes with **improved oxidative stability** and **improved CEI composition** is key to achieve long-term cycling stability.

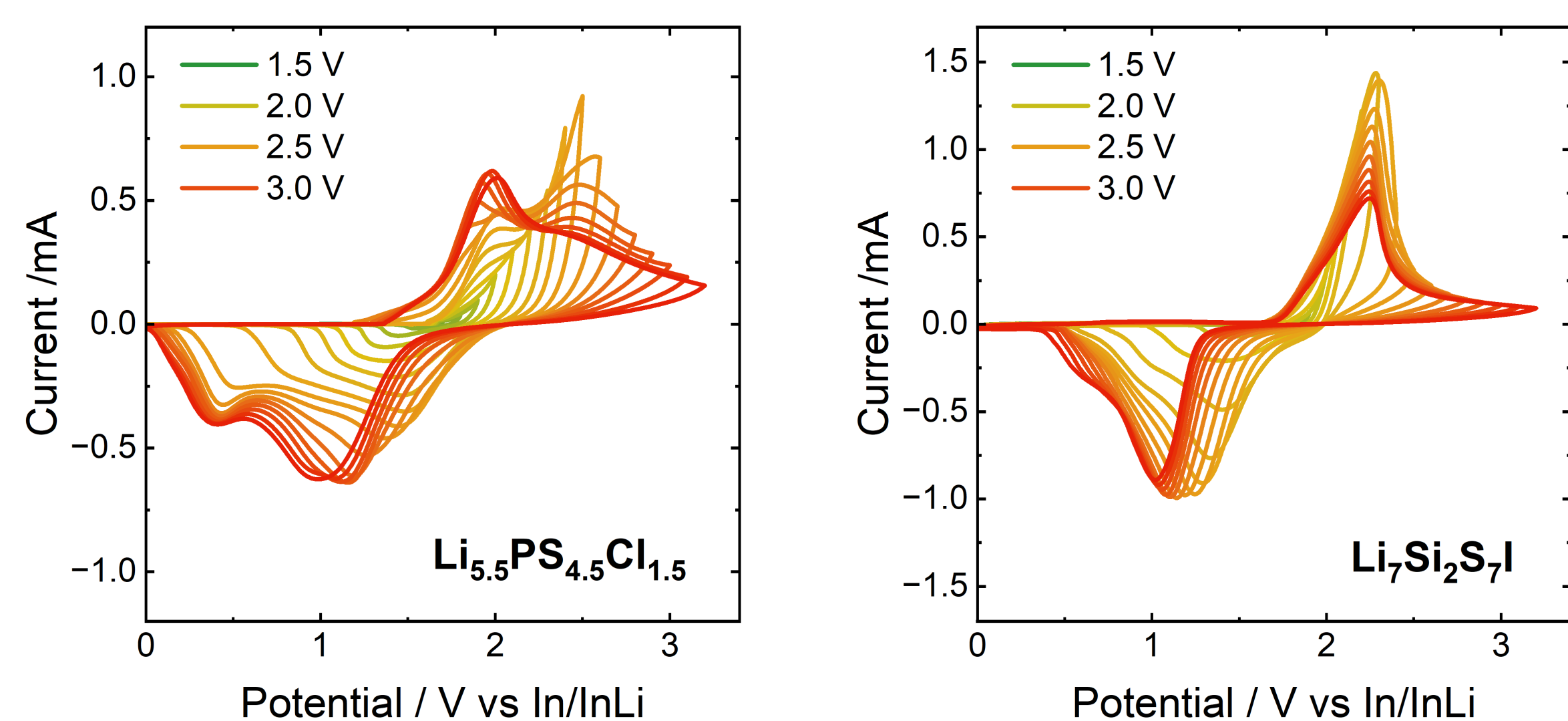


Oxidative stability of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$

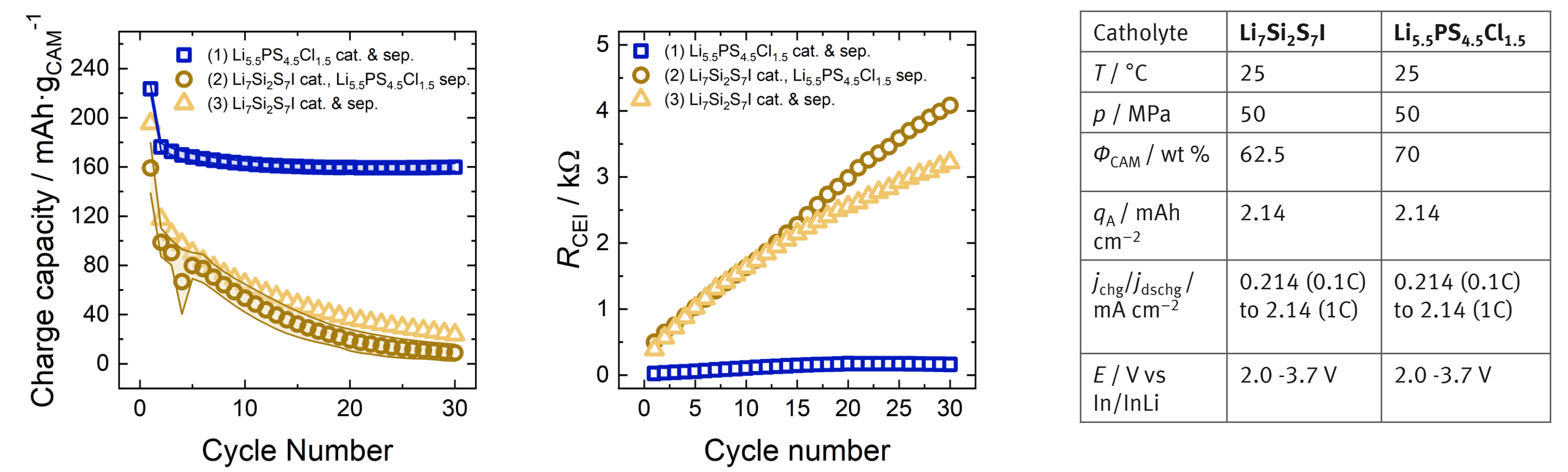
Comparison of the oxidative stability by step-wise cyclic voltammetry reveals similar onset of non-capacitive current for the **novel solid electrolyte $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$** compared to the **established lithium argyrodite $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$** .



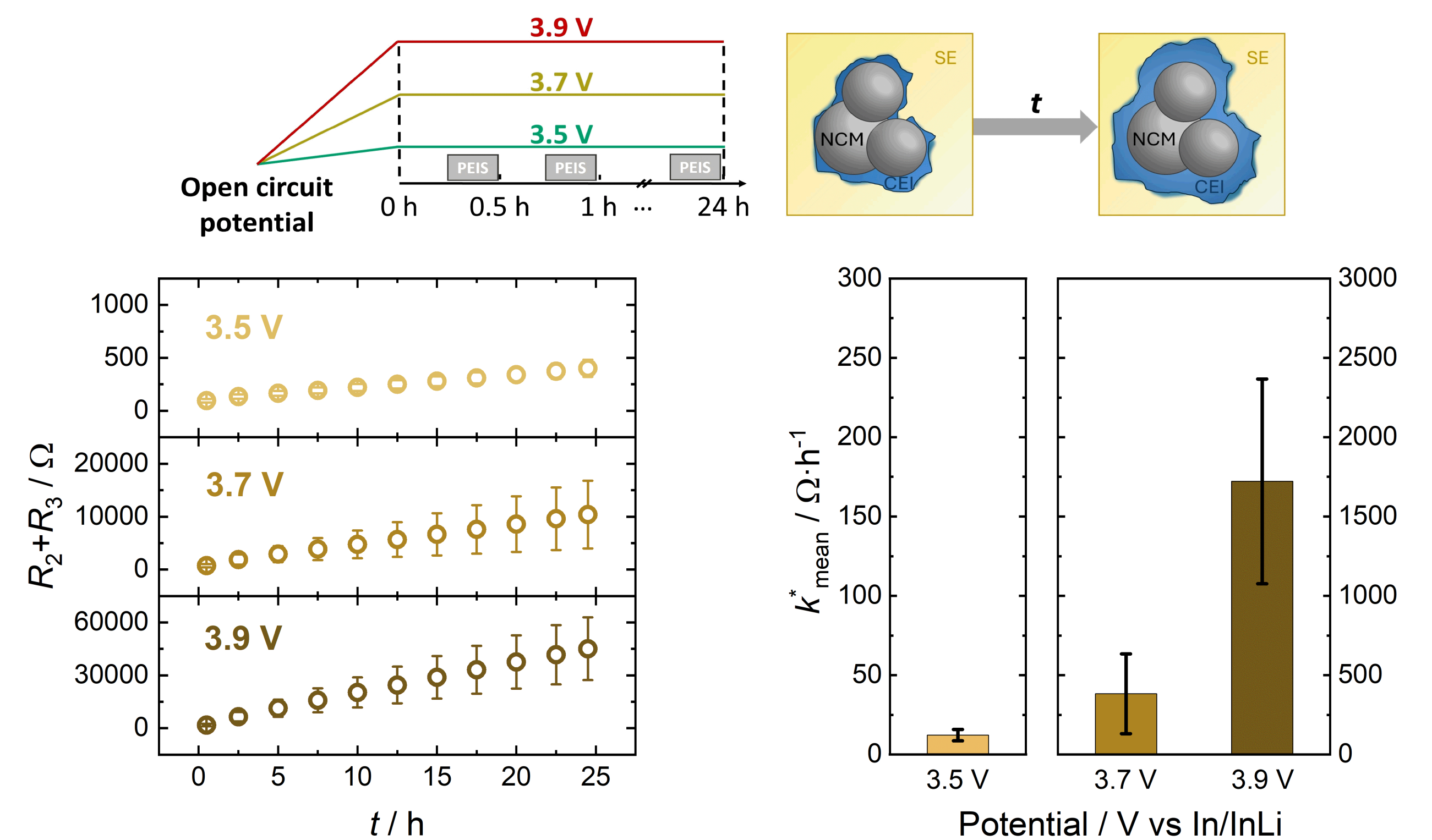
While the anionic framework of $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$ contains S^{2-} and PS_4^{3-} , that of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ is composed of pyro-thiodisilicate polyanions $\text{Si}_2\text{S}_7^{6-}$. Both solid electrolytes demonstrate highly reversible redox activity with features consistent with reversible sulfur redox as in Li-S batteries.



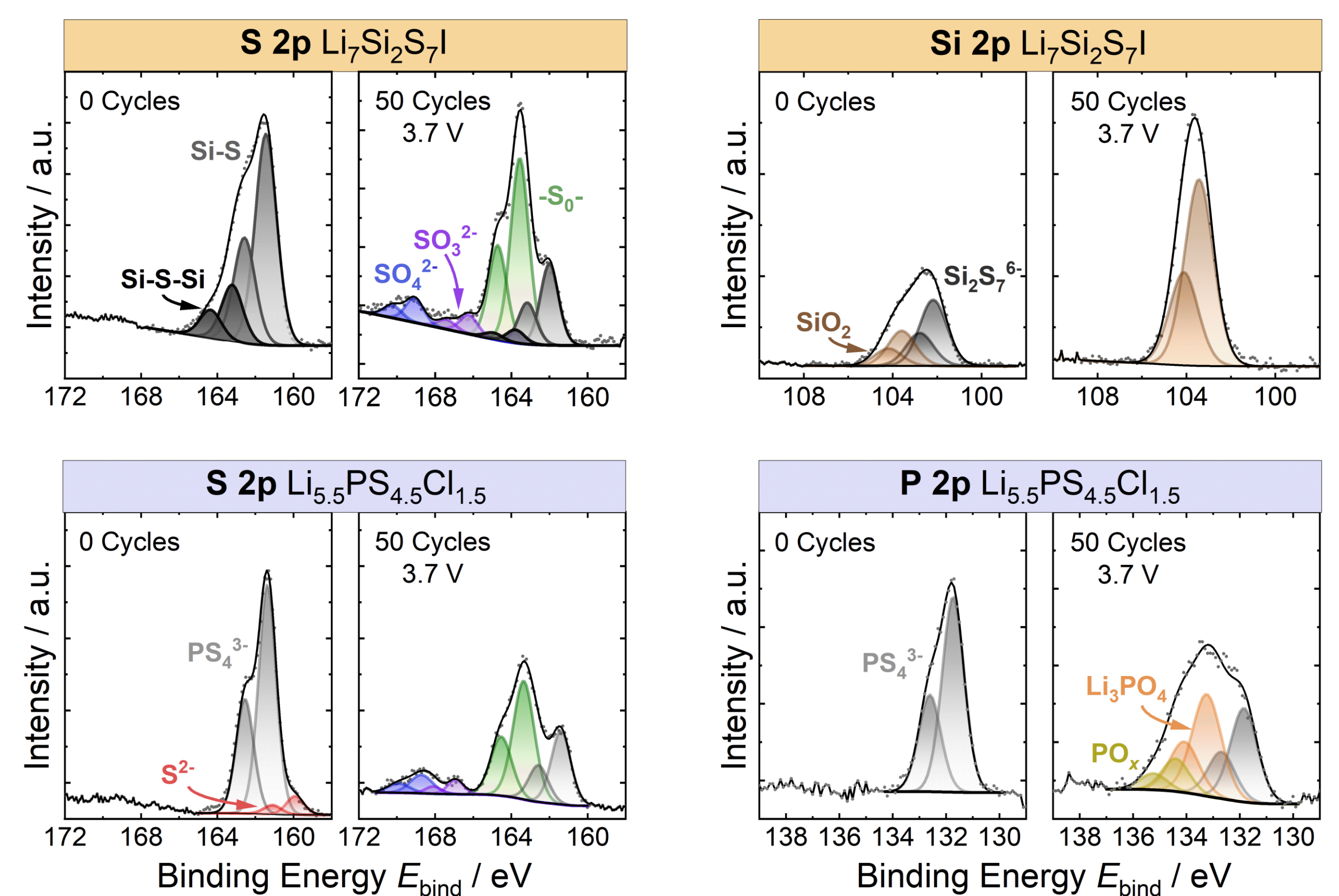
Diverging cycling behavior in NCM- and sulfur-based composite cathodes



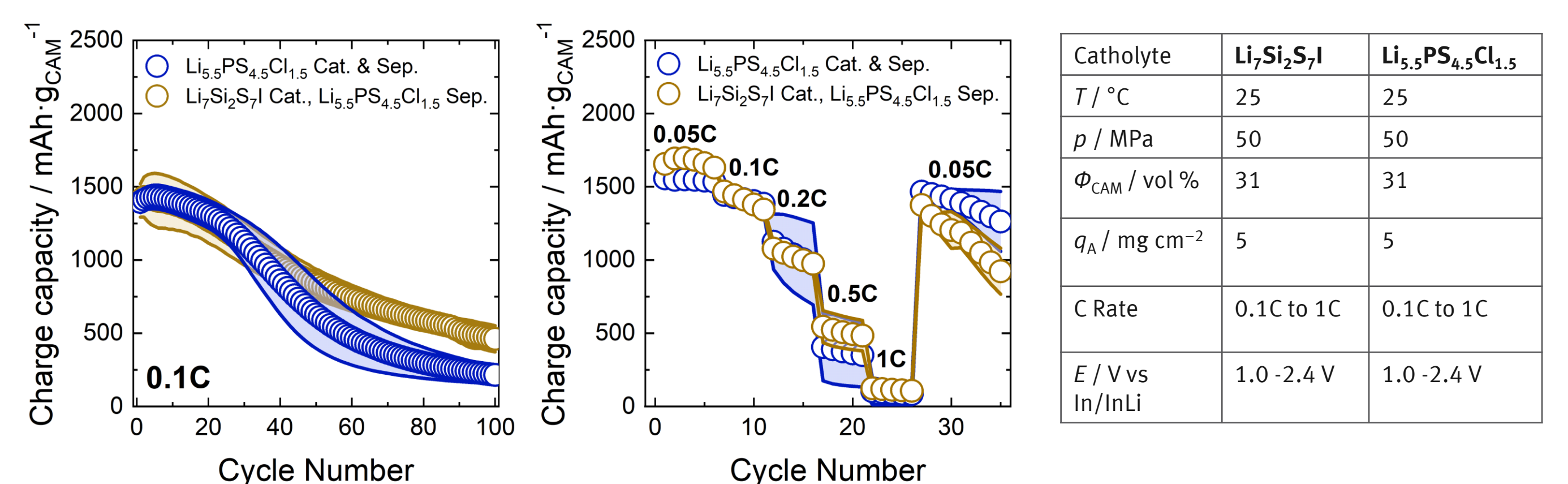
Significantly faster capacity fading when using $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ as solid electrolyte in **NCM-based composite cathodes** as a result of **high CEI resistances**.



Fast **kinetics of CEI formation**, highly dependent on the cutoff potential are revealed for NCM- $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ composite cathodes by studies using potentiostatic electrochemical impedance spectroscopy.



X-ray photoelectron spectroscopy reveals the formation of **insulating SiO_x** as key contributor to the CEI resistance when applying $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ electrolyte in NCM-based composite cathodes.



Using **S-C- $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$** composite cathodes leads to slightly improved long-term cycling stability over **S-C- $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$** and similar rate performance. $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ appears particularly **suitable for oxygen free cathode chemistries**.

Conclusion

The study reveals incompatibility of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ in NCM-based composite cathodes due to SiO_x formation. However, in sulfur-based composite cathodes the novel solid electrolyte shows promising performance.

Hartel, J. *et al.* "Electrochemical performance and stability of $\text{Li}_7\text{Si}_2\text{S}_7\text{I}$ solid electrolytes in solid-state battery cathode composites" *ACS Appl. Energy Mater.* **2025**.

