Weakly Solvating Electrolytes (WSEs) for Low-Temperature Zinc Batteries

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Weakly solvating electrolytes (WSEs) have emerged as a promising approach for enabling low-temperature operation in rechargeable batteries, by limiting excessive solvent coordination and modifying interfacial chemistry. Three organic zinc electrolytes were investigated using surface-enhanced infrared absorption spectroscopy (SEIRAS), surface-enhanced Raman spectroscopy (SERS), and electrochemical impedance spectroscopy (EIS), to consider the role of solvent and anion species in solvation structure and solid electrolyte interphase formation.

Zinc trifluoromethanesulfonate, $Zn(OTf)_2$, demonstrated surface-bound zinc-anion coordination with acetonitrile (ACN) solvent, describing a weakly solvating behavior constructive to low temperature applications. However, the solvation shell within the high entropy mixed organic solvent was dominated by dimethyl ether (DME), preventing anions from contributing to the cation solvation shell, as indicated by the increased presence of 'free' randomly orientated OTf^- ions. The mixed solvent demonstrated a reduced activation energy of interfacial relaxation, $E_a(f_{max})$, from 57.7 kJ/mol to 25.0 kJ/mol, from pure ACN to mixed ACN/DME/EA solvent, respectively. This is indicative of increased freedom of ion movement which could be constructive to low temperature battery use.

The hybrid $Zn(TFSI)_2$/LiTFSI WSE electrolyte showed a strong interfacial presence of coordinated anions at negative potential and reported an activation energy of 29.5 kJ/mol. The difference in solvation shell between the two salts in mixed solvent is attributed to increased electron delocalization in $TFSI^-$ compared with OTf^-, and its ability to weaken interionic interactions and partake in Zn^{2+} coordination. Collectively, these findings highlight solvation structure as a key design parameter for organic zinc electrolytes and provide mechanistic insight into interfacial behavior relevant to low-temperature zinc battery operation.