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

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Background

- Energy storage systems capable of operating reliably at low temperatures are increasingly critical for several applications, ranging from cold climate power grid support to space exploration.
- At reduced temperatures, electrolyte transport, charge transfer and solvation dynamics become severely constrained, often leading to unstable electrode interfaces and inefficient cycling.
- **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.**
- Zinc-based electrolytes offer improved safety relative to lithium-based chemistries, yet there has been limited research into their low temperature use and response to weakly solvating environments.
- This study investigates solvation structure as a key design parameter for organic zinc electrolytes and provides mechanistic insight into interfacial behavior relevant to low-temperature zinc battery operation.

Methods

- **Three organic zinc electrolytes were investigated using surface-enhanced infrared absorption spectroscopy (SEIRAS), surface-enhanced Raman spectroscopy (SERS), and electrochemical impedance spectroscopy (EIS).**
- SEIRAS and SERS are complementary surface sensitive techniques which can be used to study electrode reactions and molecular reorganizations.
- Temperature-dependent EIS demonstrates the impact of low temperature resistance and ion-transport limitations, enabling direct correlations between interfacial chemistry, impedance response, and practical low-temperature electrochemical performance.

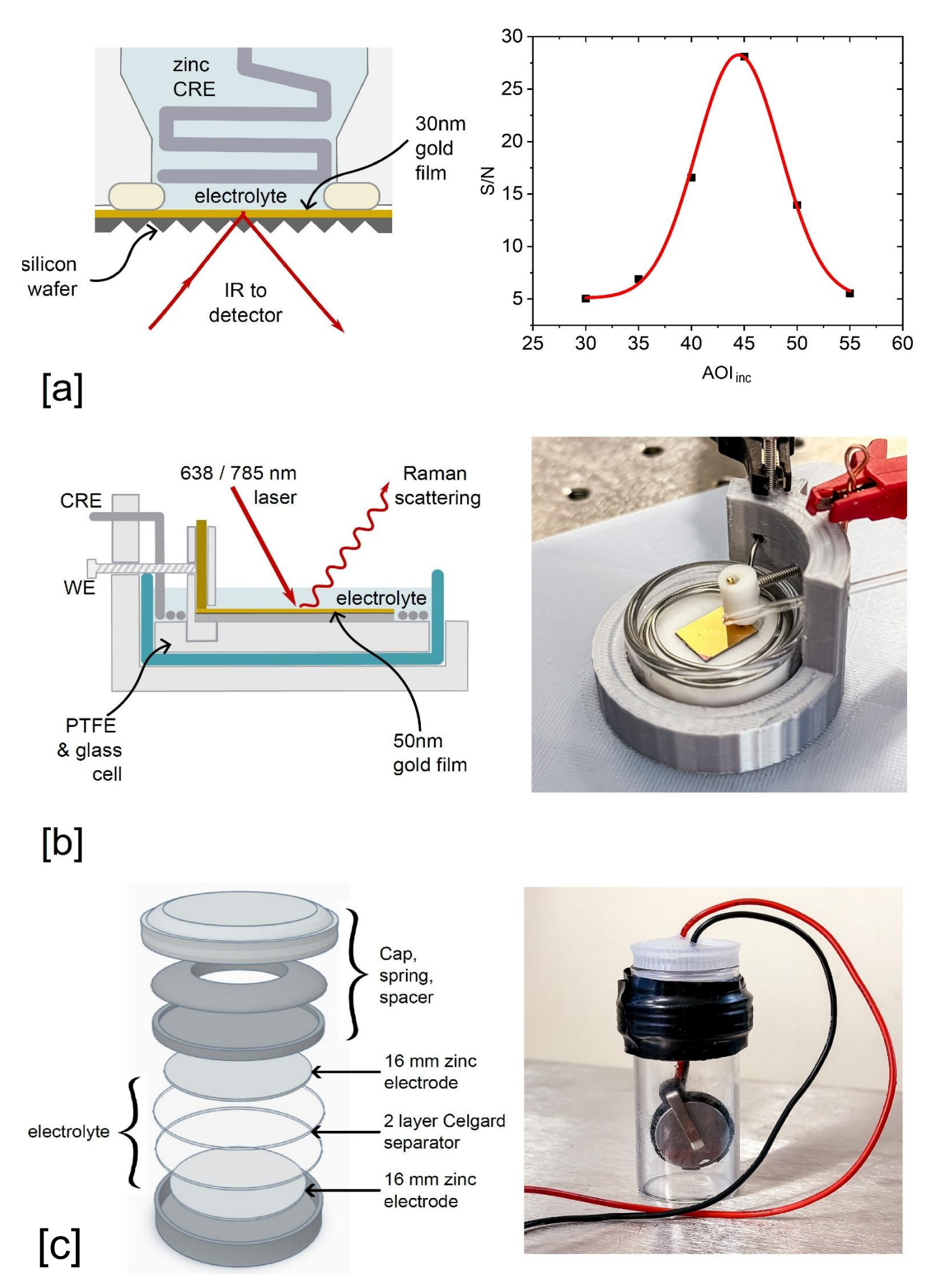

Figure 1: Experimental schematics and instrumental photographs.

[a] Left: The electrochemical SEIRAS cell, with a gold film electrode thermally evaporated onto a specialized micro-grooved silicon wafer. The IR signal is enhanced at the gold/electrolyte surface, giving surface sensitive measurements.
Right: Angle of incidence signal-to-noise ratio data for $Zn(OTF)_2$ in acetonitrile. Potential-dependent measurements were carried out at 45 °.

[b] Homemade SERS cell, using an electroplated and roughened gold film electrode to enhance Raman scattering. The Raman laser passes through a thin layer of electrolyte and is focused on the gold electrode surface.

[c] Left: Coin cell battery construction for EIS measurements. **Right:** Coin cells were tested at 20 °C, 10 °C, 0 °C, and -10 °C by submerging within a watertight vial inside a liquid chiller chamber.

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References

- Shi, X. et al. *Nat Commun* **2024**, 15 (1), 302. DOI: 10.1038/s41467-023-44615-y.
- Ren, K. et al. *ACS Energy Lett.* **2024**, *9* (6), 2960–2980. DOI: 10.1021/acsenergylett.4c00621.
- Holoubek, Jet al. *Energy Environ. Sci.* **2025**, *18* (18), 8608–8617. DOI: 10.1039/D5EE02978C.
- Zhao, Y. et al. *Chemical Engineering Journal* **2024**, *481*, 148335. DOI: 10.1016/j.cej.2023.148335.

Overview

- At low temperatures, **transported cations can become trapped by their solvent** solvation shell, reducing battery performance.
- High entropy organic solvents offer a weakly solvating environment that **disrupts the Zn^{2+} solvation shell**, improving desolvation at the electrode surface.
- WSEs also allow more cation-anion interaction within the solvation shell, leading to an **anion-based solid electrolyte interphase** (SEI) surface which protects the electrode surface from corrosion and enhances cycling performance.

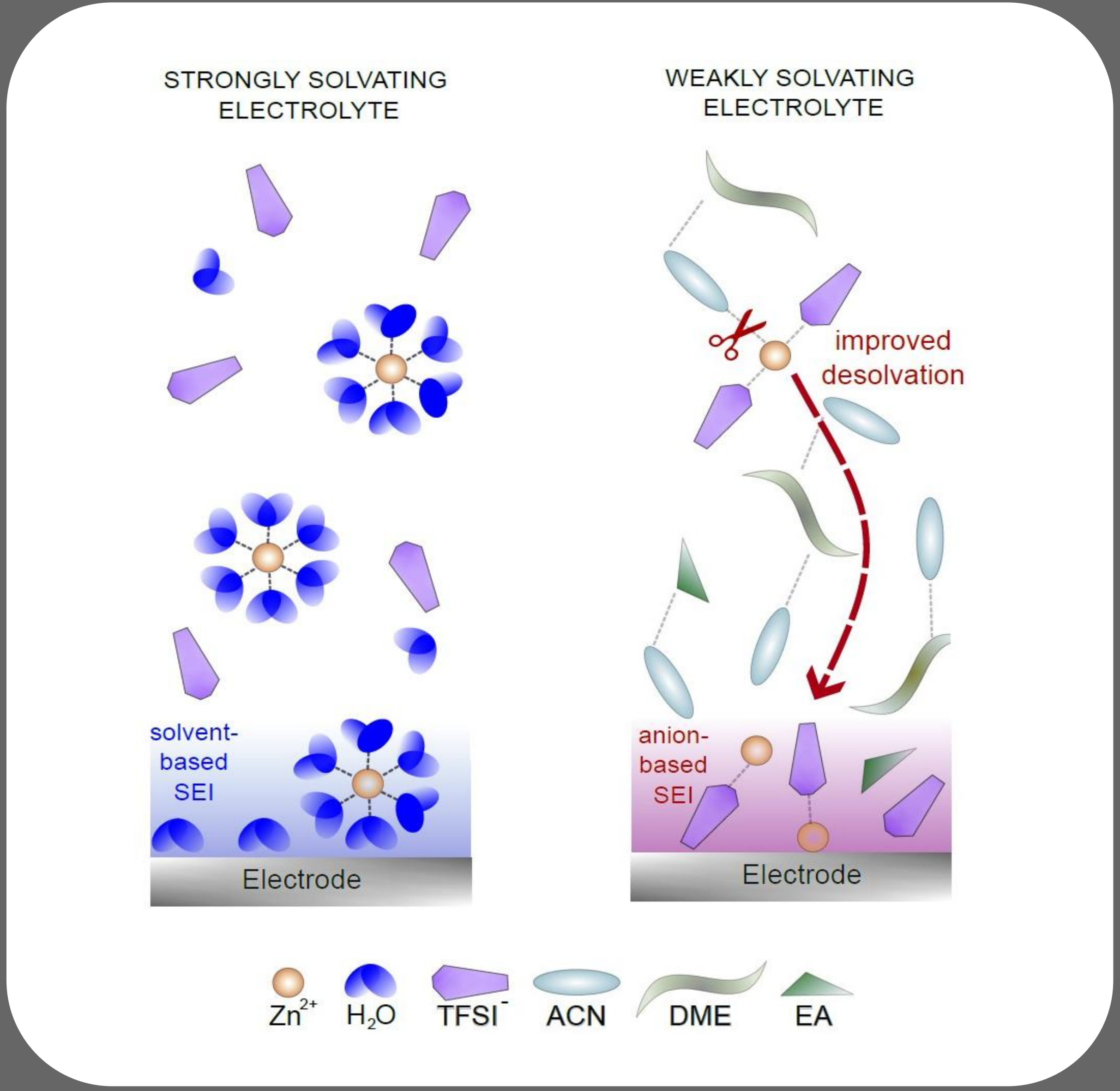

Figure 2: Concept schematic of the near- surface behavior of traditional, strongly solvating, electrolytes vs high entropy weakly solvating electrolytes (WSEs).

Conclusion

- In the organic WSE electrolytes examined, acetonitrile remains an interesting solvent, particularly when combined with $Zn(OTf)_2$ salt. Its weakly solvating qualities allow anions to partake in cation solvation, which is desirable in the formation of functional electrode SEI layers.
- The mixed ACN/DME/EA solvent tested was more suited to the coordination matrix of $Zn(TFSI)_2$, allowing for an anion-based ZnF_2 rich SEI layer. The $Zn(OTf)_2$ solvation shell was dominated by the DME in this mixed solvent, and high double layer capacitance led to undesirable ion accumulation at the electrode.
- The mixed solvent demonstrated low activation energies of interfacial relaxation compared with pure ACN, suggesting increased freedom of ion movement due to high entropy disruption of ion interactions, in keeping with the WSE concept.
- These findings demonstrate that weakly solvating, organic electrolytes fundamentally reshape zinc solvation and interfacial chemistry and can promote anion influenced SEI formation. This solvation driven approach provides a viable framework for achieving stable zinc electrochemistry at low temperatures.

$Zn(OTf)_2$ = zinc trifluoromethanesulfonate, $Zn(TFSI)_2$ = zinc bis(trifluoromethylsulfonyl)imide ACN = acetonitrile, DME = dimethyl ether, EA = ethyl acetate

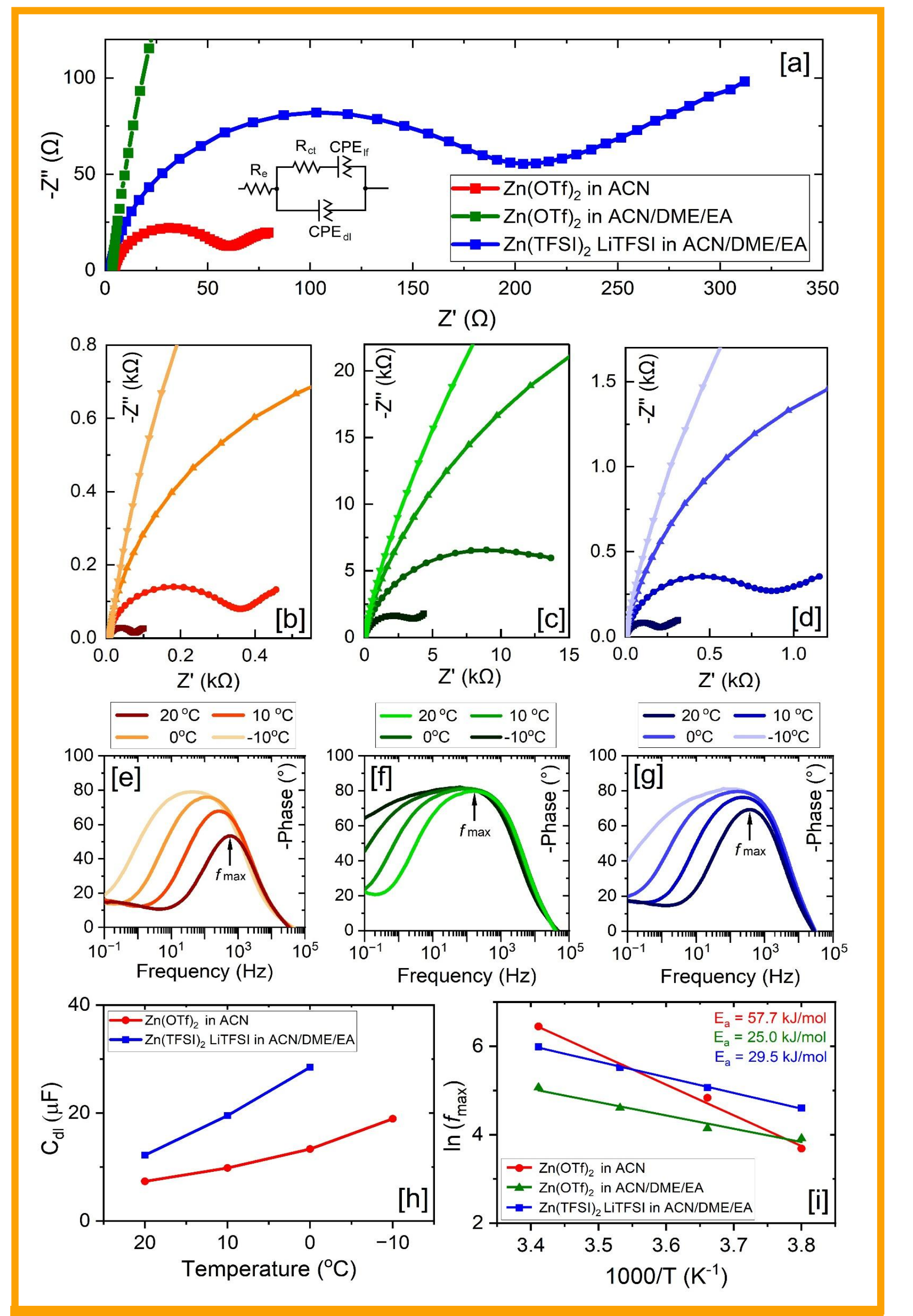

Figure 3: EIS measurements. [a] Nyquist plots and circuit model for at 20 °C. [b]-[g] Temperature-dependent (20 °C to -10 °C) Nyquist and Bode plots. [h] Double layer capacitance calculations. [i] Arrhenius plot for relaxation energy E_a (f_{max}).

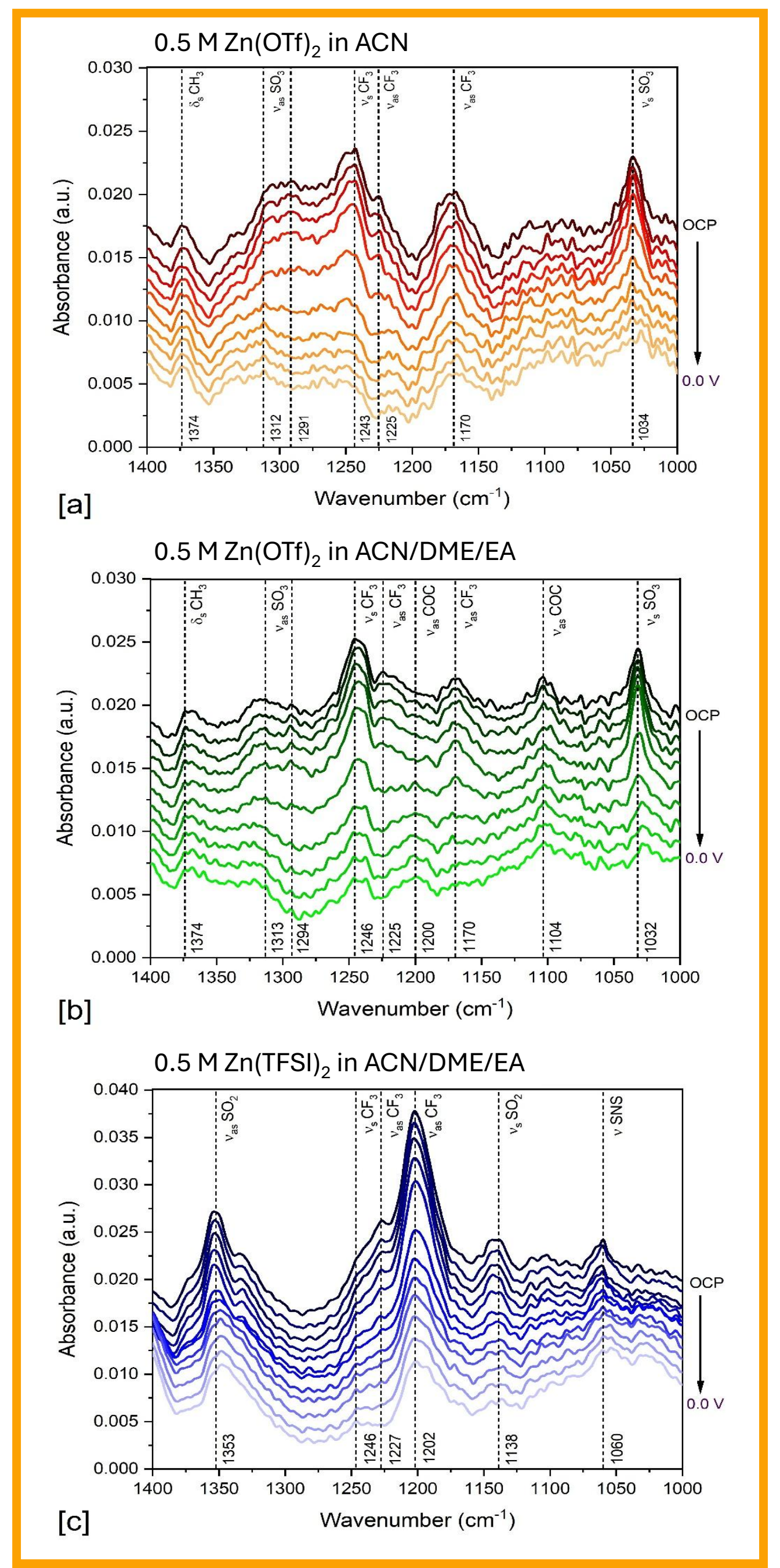

Figure 4: Potential-dependent SEIRAS spectra, taken in increments of 0.1 V from open circuit potential (OCP) to 0 V, for three organic zinc electrolytes.

Results

- EIS circuit modelling allowed calculated activation energies of interfacial relaxation, E_a (f_{max}), of 57.7 kJ/mol and 25.0 kJ/mol for $Zn(OTf)_2$ in ACN and mixed ACN/DME/EA solvent respectively, while the $Zn(TFSI)_2/Li(TFSI)$ hybrid electrolyte achieved 29.5 kJ/mol.
- **The SEIRAS spectra for $Zn(OTf)_2$ in ACN showed a dominance of asymmetric anion molecular vibrational modes at negative potential, suggesting anions can contribute to the solvation shell, in keeping with the WSE concept.**
- When dissolved in mixed ACN/DME/EA solvent, $Zn(OTf)_2$ demonstrated increased presence of ‘free’, randomly orientated as DME appeared to take the place of anions within the solvation shell.
- **SERS spectra of $Zn(TFSI)_2$/LiTFSI hybrid electrolyte in mixed solvent demonstrated the presence of a ZnF_2-based SEI layer.**

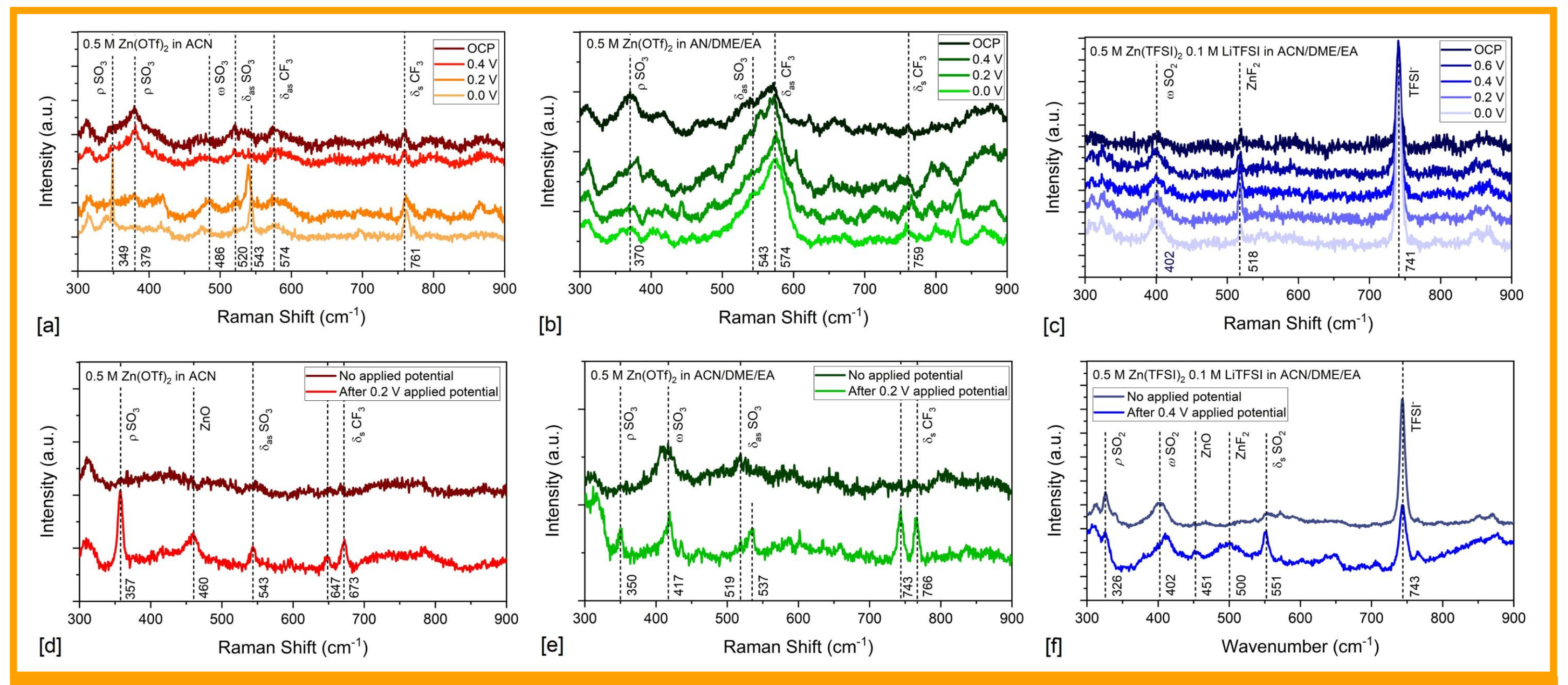

Figure 5: Potential-dependent in-situ SERS spectra for [a] 0.5 M $Zn(OTf)_2$ in ACN, [b] 0.5 M $Zn(OTf)_2$ in ACN/DME/EA, with comparable ex-situ Raman spectra displayed [d]-[f] below.