Enhancing Interfacial Capacitance in Ionic Liquid Electrolyte Blends

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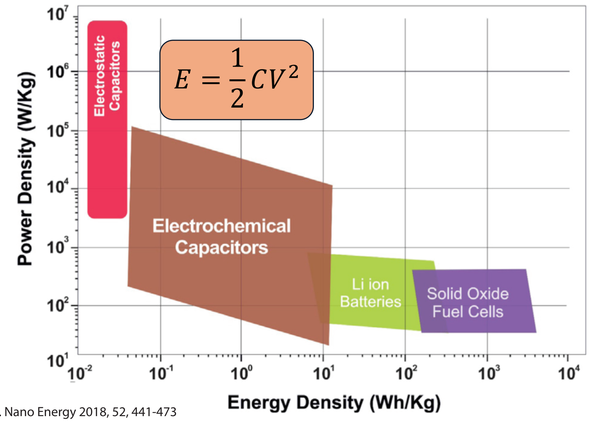
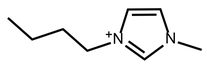
Ionic Liquid-Based Electrolytes for Supercapacitors

While supercapacitors charge and discharge over short time scales, device energy density must be increased to transition towards using renewable energy.

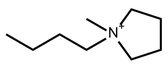


Raza et al. Nano Energy 2018, 52, 441-473

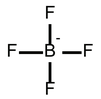
Ionic liquids (ILs) show promise as next-generation supercapacitor electrolytes due to their nonflammability, tunability, and wide electrochemical stability windows.



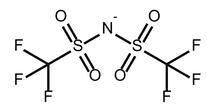
1-butyl-3-methylimidazolium [C_4MIm]



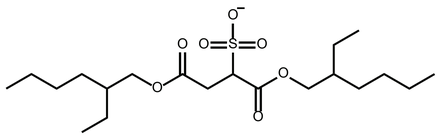
1-butyl-1-methylpyrrolidinium [C_4MPyrr]



tetrafluoroborate [BF_4]



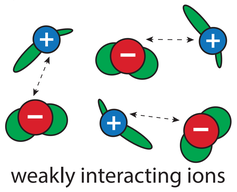
bis(trifluoromethanesulfonyl)imide [TFSI]



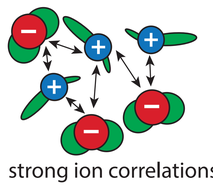
1,4-bis-2-ethylhexylsulfosuccinate [AOT]

Correlations in Neat Ionic Liquids

While high ion concentrations suggest high capacitances, ILs have low experimental capacitances compared to aqueous and organic electrolytes due to bulk ion correlations.

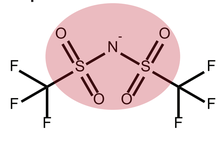


weakly interacting ions (aqueous or organic electrolytes)

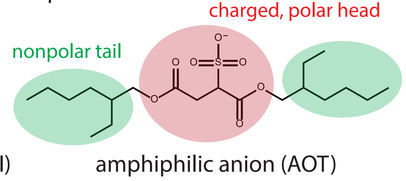


strong ion correlations (ionic liquid electrolytes)

Correlations present an opportunity to tune molecular interactions in ionic liquids to raise interfacial capacitance.

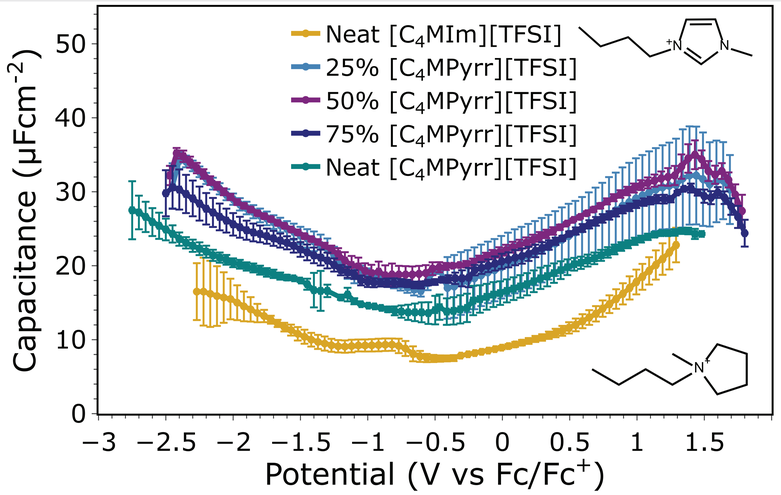


non-amphiphilic anion (TFSI)

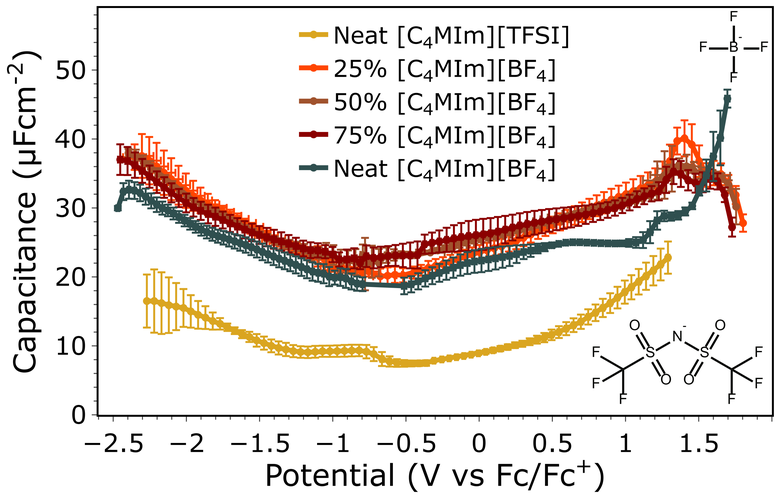


amphiphilic anion (AOT)

Non-Amphiphilic IL Mixtures Exhibit Capacitive Increase on Glassy Carbon Surface



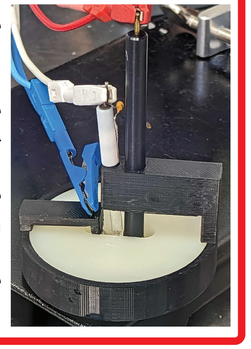
While blends of [C_4MPyrr][TFSI] and [C_4MIm][TFSI] containing two cation cores are expected to influence primarily negative potentials, ion packing improves capacitance in mixtures over the entire window as compared to either neat IL.



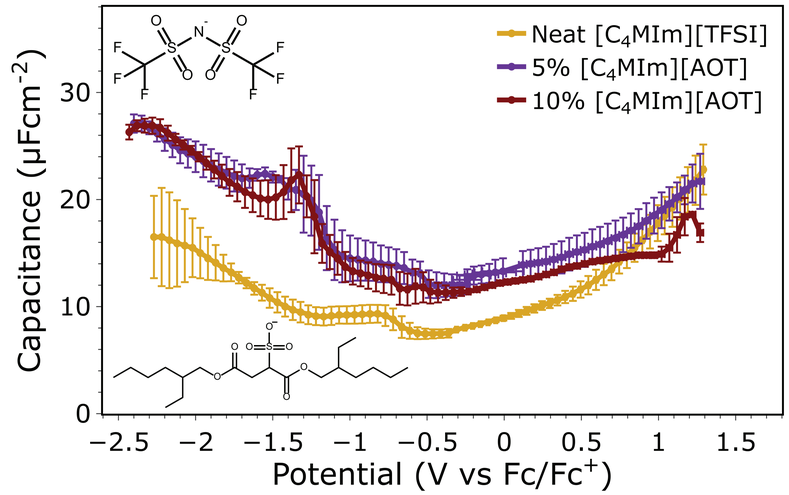
Amplified capacitance in mixtures of [C_4MIm][BF_4] and [C_4MIm][TFSI] suggests tuning ionic correlations nontrivially influences surface structuring.

Methods

- Cyclic voltammetry was utilized to determine the stability window of each electrolyte.
- Potential-dependent capacitance was evaluated using electrochemical impedance spectroscopy over the entire electrolyte stability window using a three-electrode setup.
- [C_4MIm][AOT] was synthesized via ion exchange between [C_4MIm][Cl] and [Na][AOT] dissolved entirely in dichloromethane.
- All remaining ionic liquids and metal salts were commercially available and purified before use.

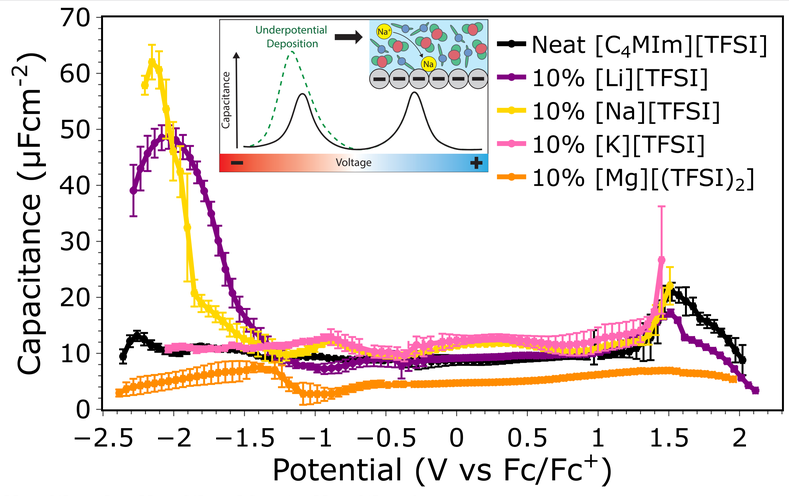


Amphiphilic Anions Enhance Capacitance on Negative Glassy Carbon Surface



Weaker correlations between the amphiphilic anion AOT and C_4MIm selectively increase capacitance over one half of the electrochemical window.

Capacitive Enhancement in Salt-in-Ionic Liquid Electrolytes on Negative Gold Surface



[Li][TFSI] or [Na][TFSI] in [C_4MIm][TFSI] enhances capacitance at a negative gold surface as a result of underpotential deposition.

Summary

- Adding the amphiphilic anion AOT selectively enhances cathodic capacitance.
- The electrode-electrolyte interface can be engineered to promote favorable ion packing and surface reactions for electrochemical energy storage.

Acknowledgements

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