XXV MEETING OF PHYSICS

First-Principles Investigation of Electrolyte–Electrode Interfaces: From Lithium Metal to Sodiated MoS_2

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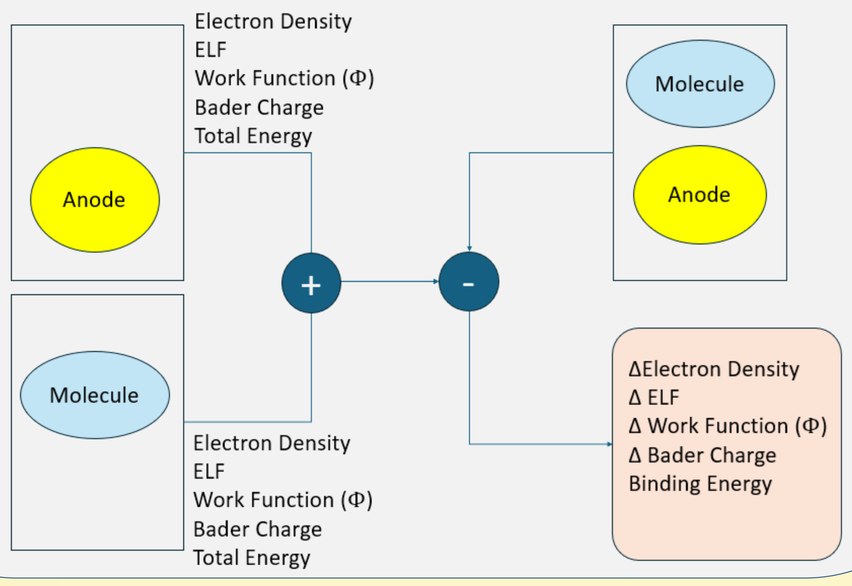
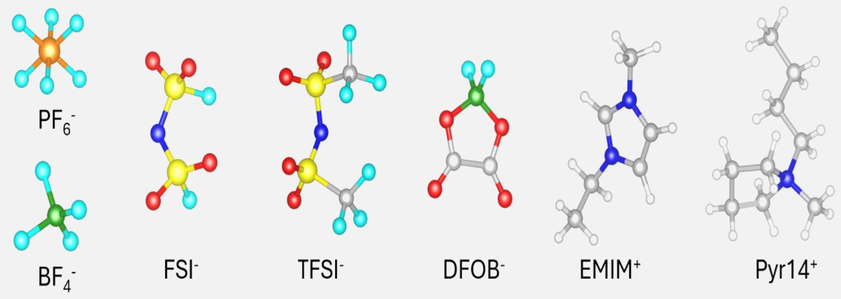
Introduction and Methodology

Lithium-metal batteries offer high energy density, but the highly reactive Li-metal anode poses significant challenges for interfacial stability. Ionic liquids (ILs) offer safer and more stable electrolyte alternatives; however, their molecular interactions with Li-metal play a critical role in the formation and properties of the solid electrolyte interphase (SEI), ultimately affecting battery performance. In parallel, MoS_2 is a promising anode material for sodium-ion batteries due to its high theoretical capacity and favorable layered structure. Understanding the interactions between ionic liquid electrolytes and MoS_2 is therefore essential for elucidating interfacial stability and sodium-storage mechanisms in next-generation Na-ion batteries.



Objective



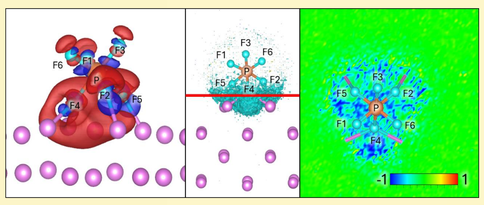
Analyze through DFT simulations, the reactivity and interfacial stability of ionic liquid cations ($EMIM^+$, $Pyr14^+$) and anions (FSI^-, $TFSI^-$, $PF6^-$, $BF4^-$, $DFOB^-$) on Li-metal and MoS_2 surfaces, using electronic and energetic descriptors to guide the design of safer and more efficient electrolytes for next-generation energy-storage systems. Li-metal anodes offer the highest theoretical specific capacity (3862 mAh g^{-1}), far exceeding that of graphite (~372 mAh g^{-1}), while MoS_2 is a promising anode material for sodium-ion batteries, with a theoretical capacity of approximately 670 mAh g^{-1}. The high reactivity of Li-metal and the electrochemical activity of MoS_2 require a detailed understanding of their interactions with advanced electrolytes such as ionic liquids (ILs).

Li-metal

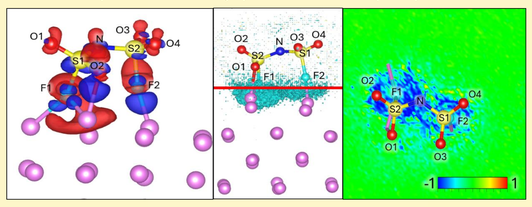
MoS_2

Results and Discussion

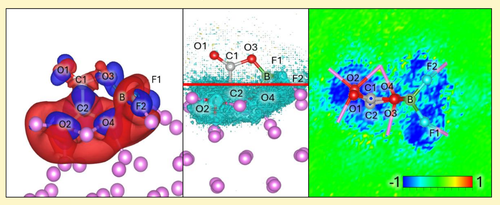
Hexafluorophosphate anion (PF_6^-)



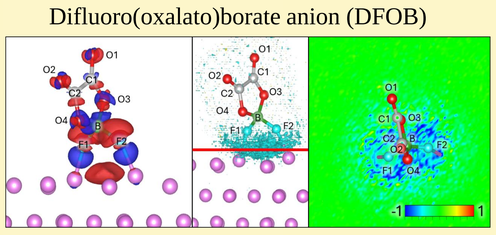
Bis(fluorosulfonyl)imide anion (FSI)



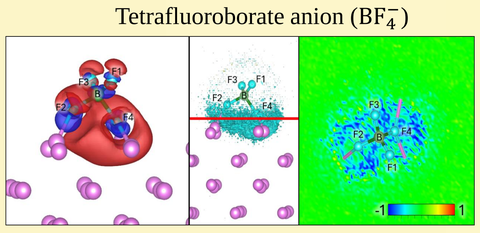
Difluoro(oxalato)borate anion (DFOB)



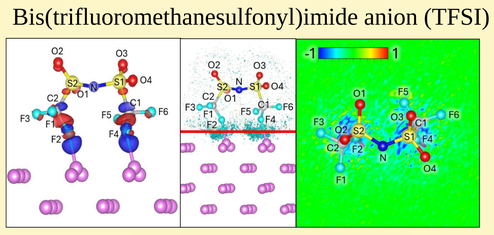
Difluoro(oxalato)borate anion (DFOB)



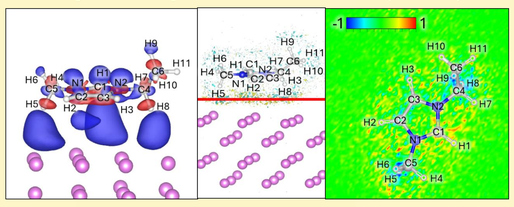
Tetrafluoroborate anion (BF_4^-)



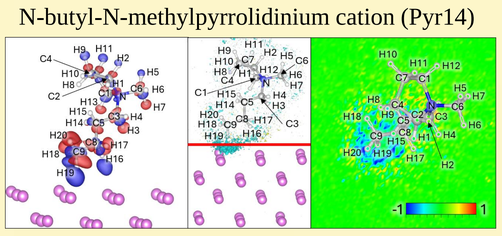
Bis(trifluoromethanesulfonyl)imide anion (TFSI)



1-ethyl-3-methylimidazolium cation (EMIM)



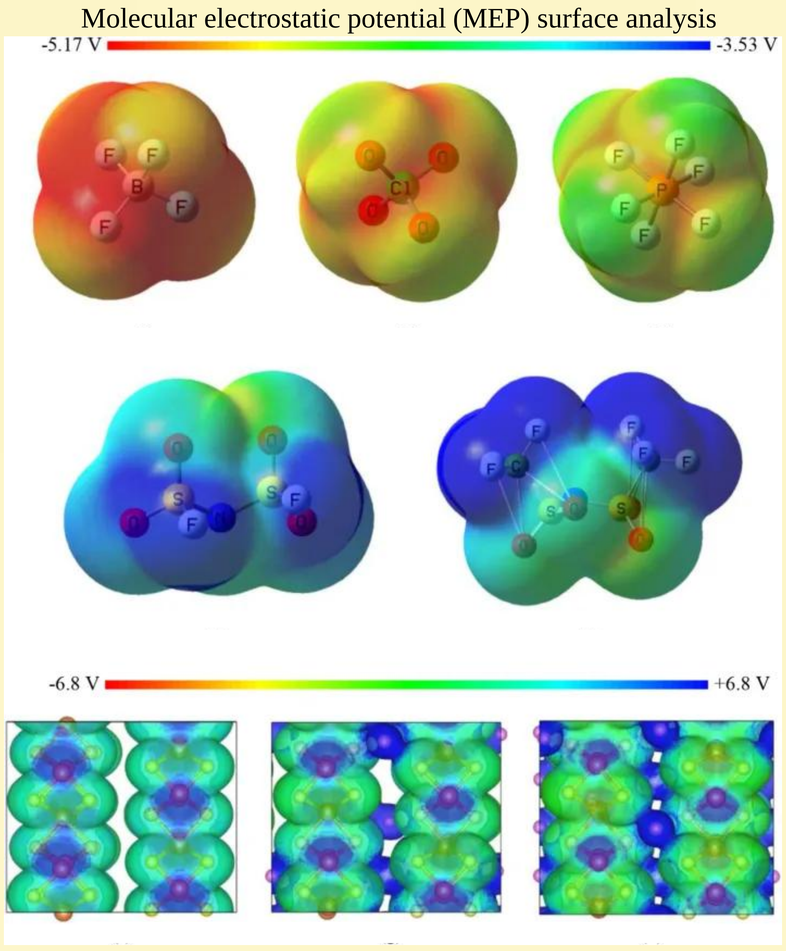
N-butyl-N-methylpyrrolidinium cation (Pyr14)



Calculated adsorption properties on a Li-metal surface for multiple molecular orientations. The total slab–molecule energy, binding energy, molecular net charge, charge transfer, and work function change (ΔΦ)

Molecule	Attack Orientation	Total Molecule/Slab Energy (Ry)	Binding energy (eV)	Molecule charge	Charge transfer	ΔΦ
PF6	3F	-953.9407	2.15	-1.371	-0.371	-2.389
BF4	3F	-791.1409	2.35	-1.282	-0.282	-2.410
FSI	3O	-987.8320	2.09	-1.308	-0.308	-1.873
	2O–F	-987.7712	1.38	-1.312	-0.312	-1.871
	2F	-987.7769	1.65	-1.398	-0.398	-1.855
TFSI	FO	-1262.0411	1.14	-1.193	-0.194	-1.828
	3O	-1262.1048	2.09	-1.358	-0.358	-2.070
	2F	-1262.0032	0.62	-1.213	-0.213	-2.018
	F–2O	-1262.0593	1.37	-1.308	-0.308	-2.070
	2O	-1262.0876	1.91	-1.419	-0.419	-2.066
DFOB	2F	-875.7581	1.47	-1.189	-0.189	-2.199
	2O	-875.7971	2.02	-1.387	-0.387	-2.154
	2F–2O	-875.9489	7.43	-3.154	-2.154	-2.289
EMIM	2H	-721.2826	2.16	0.466	-0.534	2.524
	3H	-721.2796	1.90	0.530	-0.470	1.937
	4H	-721.2801	1.91	0.497	-0.503	1.825
	6H	-721.2839	2.23	0.447	-0.553	1.937
Pyr14	4H	-721.2826	2.16	0.505	-0.495	2.119
	2H	-721.2796	1.90	0.496	-0.504	1.277
	3H	-721.2801	1.92	0.545	-0.455	2.234
	5H	-721.2839	2.24	0.471	-0.529	1.894

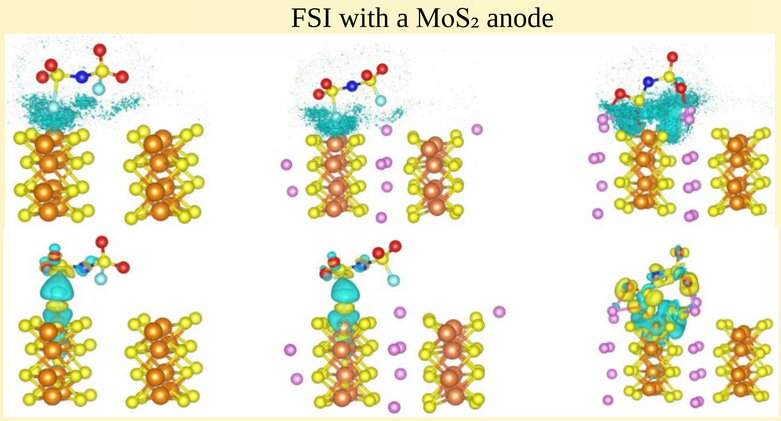
Molecular electrostatic potential (MEP) surface analysis



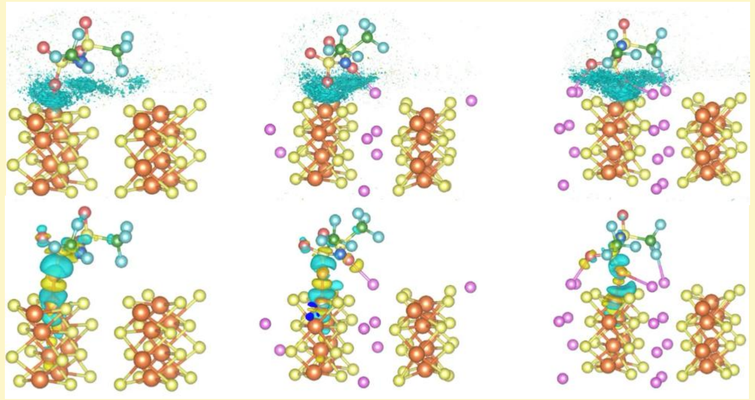
Conclusions

- First-principles and atomistic simulations reveal key trends in electrolyte–electrode interactions, charge transfer, and interfacial stability at Li-metal and MoS_2 interfaces.
- Anions (PF_6^-, BF_4^-, FSI^-, $TFSI^-$, $DFOB^-$) show strong, orientation-dependent interactions and bond weakening, while cations ($EMIM^+$, Pyr_{14}^+) mainly exhibit electrostatic interactions without significant bond breaking.
- MEP analysis identifies favorable electrostatic regions and helps explain molecular orientation, but the actual interaction depends on the combined ion–electrode electronic structure.
- FSI^- and $TFSI^-$ exhibit distinct reactivity, with $TFSI^-$ showing greater stability and FSI^- greater bond activation.
- Ion chemistry, molecular orientation, and electrode structure govern interfacial stability and SEI formation, providing insights for designing more stable Li- and Na-ion battery electrolytes.

FSI with a MoS_2 anode



TFSI with a MoS_2 anode



Paper 1 Link — *crystals* — **Paper 2 Link**

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