Adhesive Binders for High Capacity Li-ion Batteries

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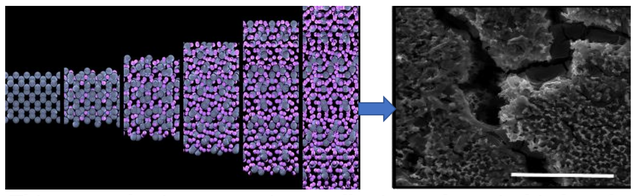
Motivation

Problems

Volume Expansion ~300%

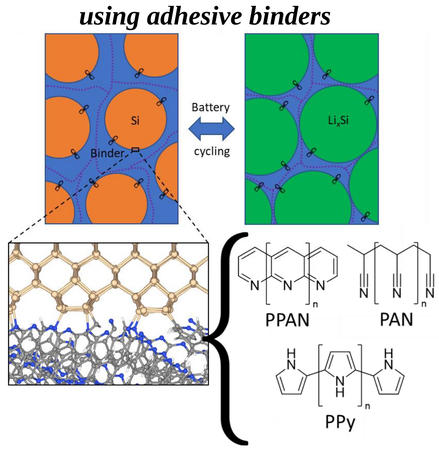
Mechanical and Electrical Failure



This research aims to engineer adhesive polymeric binders for high energy density battery electrodes, such as silicon (Si), which currently face the challenge of catastrophic mechanical and electrical failure due to large volume expansion that occurs during lithiation. Adhesive binders can potentially retain the integrity of material by forming strong and stable interfaces with Si. Pyrolyzed polyacrylonitrile (PPAN) polyacrylonitrile (PAN), polypyrrole (PPy) were investigated for their interfacial properties in this study.

Potential solution

Strong and stable interfaces using adhesive binders



Methods

Molecular Dynamics simulations using Si/C/N/H ReaxFF force field

- We have developed a ReaxFF reactive force field to study Si/C/N/H based interfaces. Previous C/N/H, Si/C/H, and Si/N/H parameters were merged, and new Si/N bond and Si/N/C valence angle parameters were developed and trained against training set generated with density functional theory (DFT).
- MD simulations were performed using LAMMPS and DFT simulations were performed using VASP.

ReaxFF potential

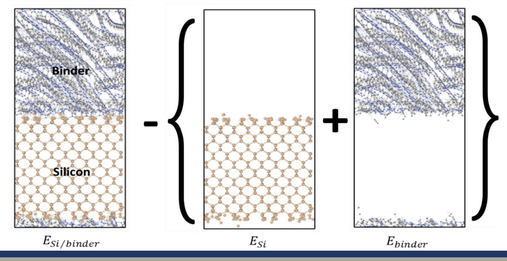
$$E_{pot}(r) = \underbrace{E_{bond} + E_{angle} + E_{tors} + E_{over} + E_{under} + E_{lp}}_{\text{Bonding}} + \underbrace{E_{vdW} + E_{Coulomb}}_{\text{Non-bonding}}$$

Mechanical properties

Binder	Density (g cm^{-3})			Young's modulus (GPa)		
	This study	Literature		This study	Literature	
PPAN	1.433 ± 0.012	1.34 – 2.1	[4]	1.184 ± 0.071	1.34	[4]
PAN	1.203 ± 0.004	1.23	[5]	6.002 ± 0.048	6.30	[7]
PPy	1.263 ± 0.007	1.25	[6]	2.059 ± 0.026	1.2-3.2	[8]

Interfacial properties

$$E_{adhesion} = E_{Si/binder} - E_{Si} - E_{binder}$$



Results

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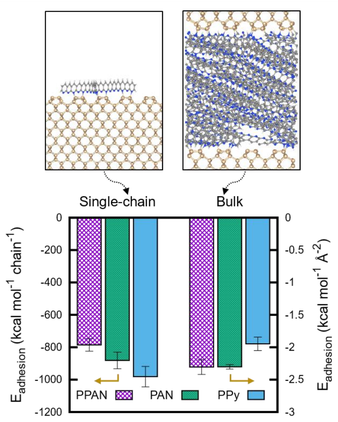
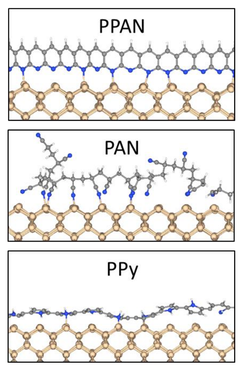


Single-chain: PPy binds stronger than PPAN and PAN

Bulk: PPy binds weaker than PPAN and PAN (**trend reversal**)

2



Single-chain: PPAN and PAN bind perpendicular and PPy binds parallel to the Si surface

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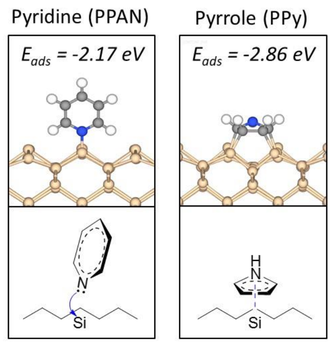

DFT (monomers): Validates observations from Si/single-chain MD simulations.

4

Possible explanations

1. Bulk polymer chains will have a similar binding mechanism and orientation as single chains of polymers on Si surface. PPAN chains orient themselves perpendicular to the surface and PPy chains orient themselves parallel to the surface.
2. The perpendicular orientation of PPAN chains allows for better alignment that allows the stacking of more chains at the interface. Fewer PPy chains can access the surface because each PPy chain lies parallel to the surface, which leads to weaker adhesion.

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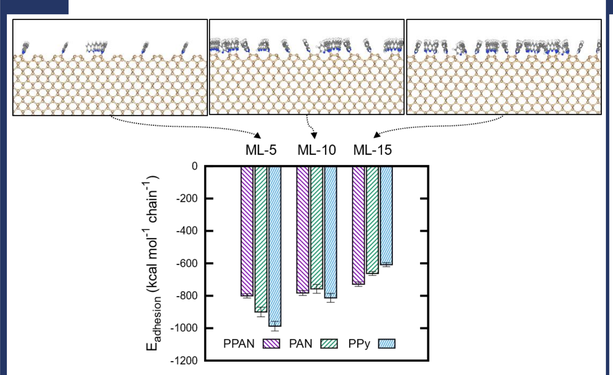

Monolayer: Adhesion energy trend reverses with increasing surface coverage (as in single-chain and bulk cases).

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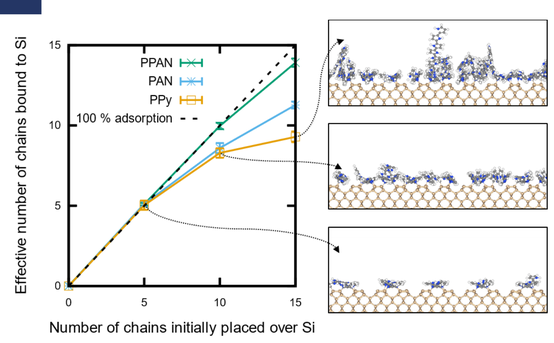

Monolayer: As the surface coverage increases, fewer PPy chains bind to Si surface as compared to PPAN.

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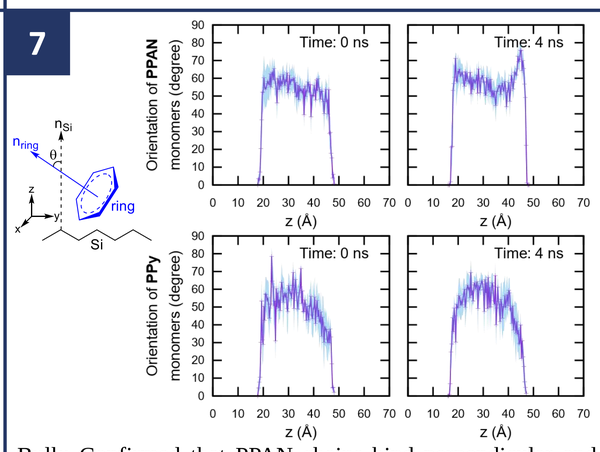

Bulk: Confirmed that PPAN chains bind perpendicular and PPy chains bind parallel to Si surface in bulk case as well.

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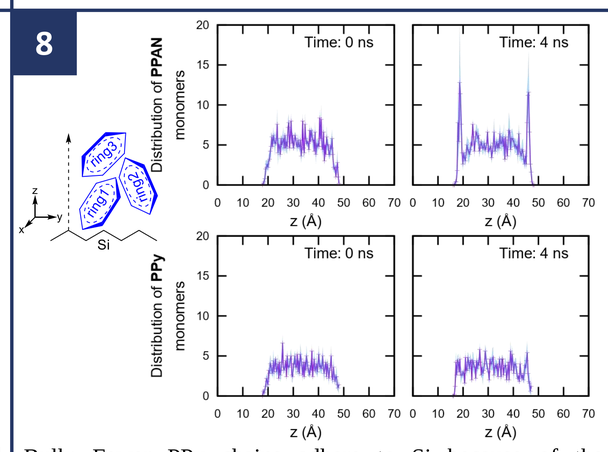

Bulk: Fewer PPy chains adhere to Si because of the increased steric crowding resulting from parallel binding nature of PPy.

Conclusions

1. Si/C/N/H force field was developed to investigate the interfacial adhesion properties of C/H/N based polymers with Si.
2. Single-chains and monomers of PPy bind stronger (in parallel orientation) to Si than those of PPAN and PAN (perpendicular orientation). Counter intuitively, bulk PPy binds weaker to Si than bulk PPAN and PAN.
3. Analysis of monolayers and bulk polymers reveal that the polymers retain their single-chain orientation in bulk phase. PPAN has perpendicular orientation and PPy has parallel orientation at Si/polymer interface.
4. Parallel (though strong) orientation of PPy causes crowding at the interface, reducing binding and adhesion.
5. Simulation methods developed provide tools to screen and design optimal binders for high-capacity batteries.

References

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