Insights into Degradation Mechanisms of Redox Flow Battery Electrodes via X-ray Absorption Spectroscopy and Classical Molecular Dynamic Simulations

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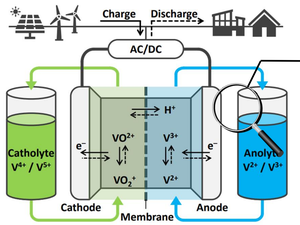
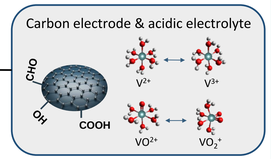
Background/Motivations

- Vanadium redox flow batteries (VRFBs) are promising candidates for stationary grid energy storage applications.
- Understanding surface functionalization is vital to address degradation during extended cycles and allow rational design of electrodes for enhanced performance.
- This project combined synchrotron-based spectroscopy techniques with advanced simulations to develop new insights into the evolution in surface chemistry of carbon electrodes in VRFBs, with an ultimate goal of providing design strategies to enhance vanadium redox reaction kinetics and durability of carbon electrodes for long-term cycling.





- Various functionalities appear during processing and post-cycling which may deteriorate cell performance.

XAS Characterization, Simulation and Interpretation

XAS characterization

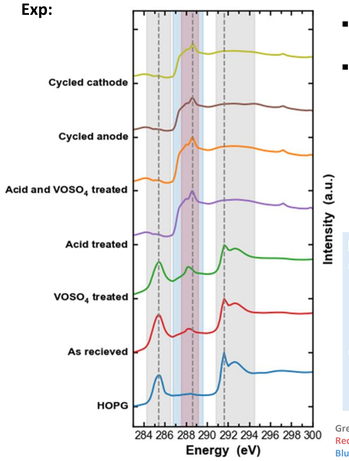
X-ray absorption spectroscopy is an element specific probe of electronic structures/bonding information/speciation, and it can be applied under both ex-situ and operando conditions.

Ex-situ carbon K-edge Near Edge X-ray Absorption Spectroscopy (NEXAFS) are obtained for:

As-received (AR) carbon electrode

- Heat treated
- Acid Solution Immersed
- $VOSO_4$ Solution Immersed
- Electrolyte Immersed
- Cycled for 1000 times

Exp:

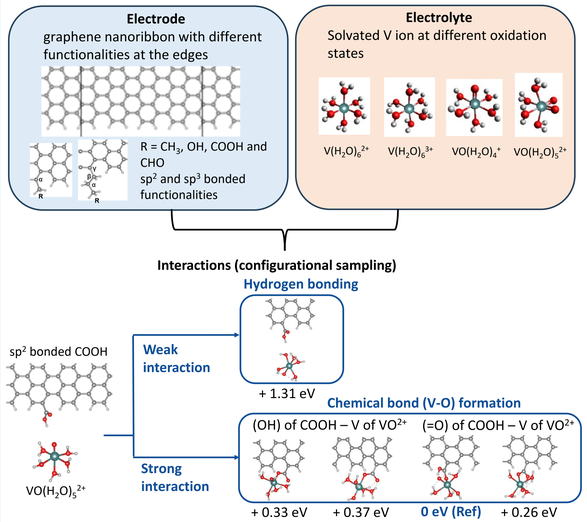


- Graphitic carbon (π* at 285 eV and σ* at 292 eV).
- Additional features between π* and σ* peaks attributed to various functionalities such as oxygen-based functionalities, including COOH and OH, which are claimed to promote V redox reaction kinetics.

Remaining unknown:
- Types and populations of functionality appeared under different treatment conditions.
- How will surface functionalities affect the performance?

Grey: π* and σ* features of graphene
Red: additional features of the as-received samples
Blue: additional features induced by acid treatment

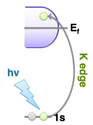
Atomistic and spectroscopy simulations



Ab initio simulations of atomic structures

- PBE-GGA projector-augmented wave (PAW) pseudopotentials.
- Polarized calculations with Hubbard U correction (U = 3.25 eV) applied to vanadium
- DFT-D3 Van der Waals correction applied.
- Ab initio molecular dynamic simulations at 300 K in NVT ensemble using Nosé-Hoover thermostat for statistical sampling.

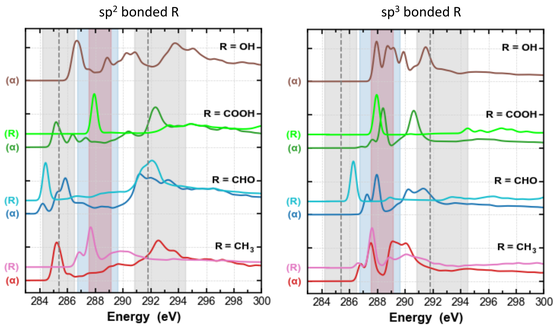
Spectroscopy simulation



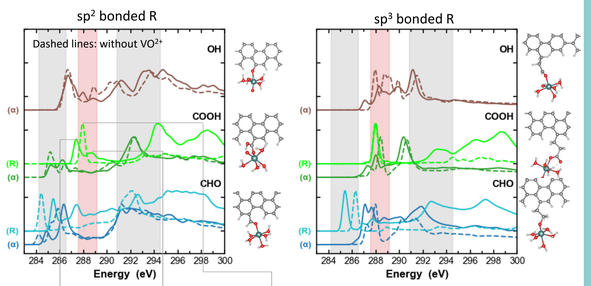
- C K edge NEXAFS are simulated for carbon atoms within the functional group and at the adsorption site of graphene nanoribbons.
- Modified pseudopotential with a 1s core electron removed is used for the exciting atom.
- Shirley reduced basis is used for efficient brillouin zone sampling.
- Excited core-hole (XCH) approximate for the final state: placing an extra electron to the lowest unoccupied states above the Fermi level.

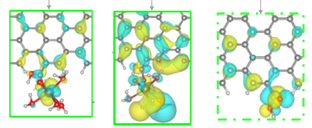
Results

Without the presence of vanadium ions



With the presence of VO^{2+}

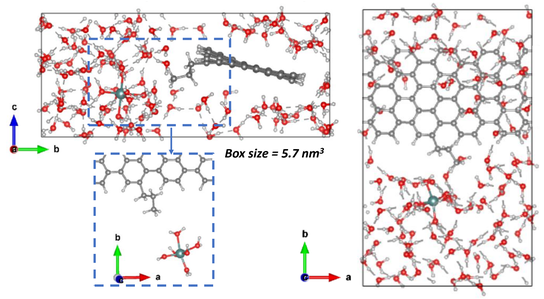


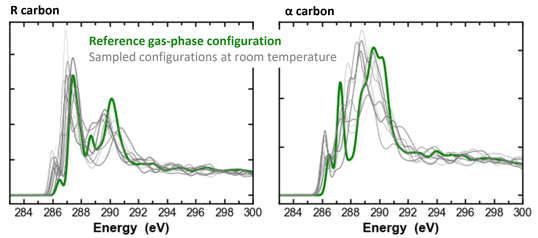


(Charge densities of the excited state contributing to specific spectroscopic signatures)

- As-received electrodes – signature at 288 eV – sp^2 bonded COOH.
- $VOSO_4$ solution immersed samples – no significant change - sp^2 bonded COOH.
- Acid treatment – significant impacts – increased population of sp^2 bonded CH_3 and COOH.

Ab-initio molecular dynamic simulation to sample the thermal effects





- Predominant features are kept in the spectra of sampled solvated structures

A library of simulated C K-edge NEXAFS is constructed for all relevant carbon atoms in distinct chemical environment.

✓ Different interaction modes between functional groups and vanadium ions.
✓ Different oxidation states of vanadium ions.

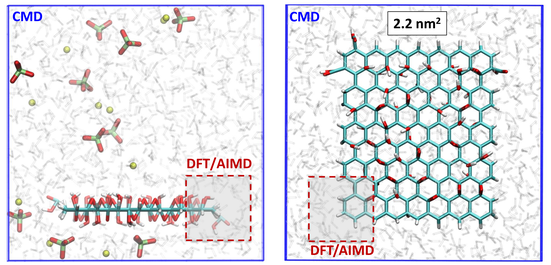
Such a library will allow unbiased interpretation of experimental spectrum collected ex-situ and in-situ for samples gone through different treatment conditions. More importantly, it can help to derive correlation between local chemistry and performance through identifications of unique functionality of the carbon electrode.

Classical Molecular Dynamic Simulation

Simulation details

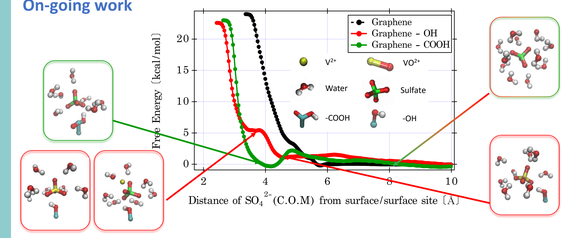
Forcefield: Lennard Jones Potential + Coulomb Energy (point charges), non-polarizable.
Graphene: *OPLS AA force field*
Vanadium: *Gupta, et al., JML - 2016*
Sulfate: *Jungwirth, 2010 and Cannon et al., 1994*
Benchmarking to ab-initio data (in progress)

Classical MD allow access to longer time and length scale with sufficient statistics



Enhanced sampling techniques
- Well-tempered metadynamics: Add potential bias to 'encourage' simulation to visit configurational space that is thermodynamically unfavored.
- Accelerating slow modes and/or chemical process with large activation barriers.

On-going work



- Surface terminations (-COOH,-OH) tend to increase the favorability of ion adsorption.
- V^{2+} is found to favor adsorption at the -OH site rather than -COOH.

Future work

- In-situ XAS characterization to probe dynamical response of the functioal groups during operation.
- Classical molecular dynamic simulations with advanced sampling to address the impact of anions and density of the functional group on V interaction with the functioanl group.
- Ab initio simulations to understand charge transfer mechanism during V redox reaction and to elucidate the role of functional groups.

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