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Crosslinked Polyethyleneimine Gel Polymer Interface to Improve Cycling Stability of RFBs

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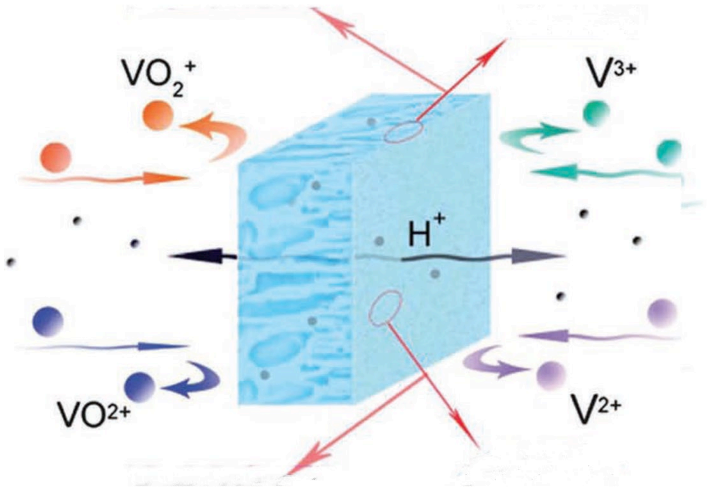
Pacific Northwest National Laboratory

Presentation # 604

U.S. DEPARTMENT OF ENERGY BATTELLE

PNNL is operated by Battelle for the U.S. Department of Energy

Redox flow battery and the membranes

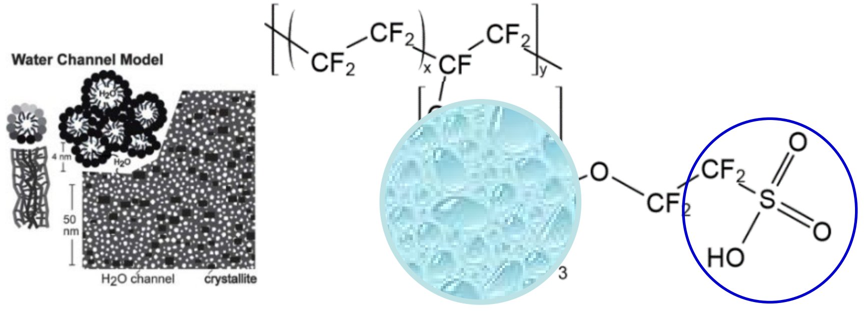


Functionality requirements
- High ionic permselectivity
- Low electric resistance
- High stability
- Low cost

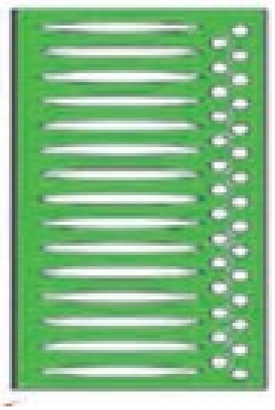
H. Z. Zhang et al. *Energy Environ. Sci*. 2011 , 4 , 1676 .

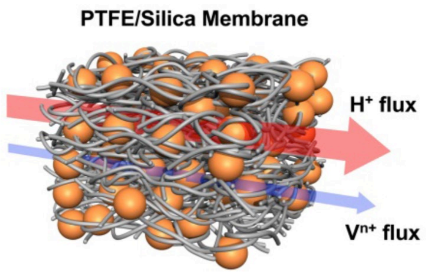
Various RFB membranes

Ion-exchange membrane



Porous separator





Perfluorinated cationic exchange membranes (Nafion™)		
Backbone	Cation exchange groups	**Advantage:** • Excellent chemical stability • High proton conductivity **Challenges:** • Vanadium crossover • Mechanical properties
tetrafluoroethylene	sulfonate vinyl ether	
Non-perfluorinated cationic exchange membranes (CEM)		
Typical Non-perfluorinated CEM		**Advantage:** • Lower cost **Challenges:** • Lack of long-term stability • Mechanical properties
sulfonated poly(aryl ketone ketone)	sulfonated poly(aryl ether sulfone)	
sulfonated poly(arylene thioether	sulfonated poly-(fluorenyl ether thioether ketone)	
sulfonated poly(arylene ether sulfone)	sulfonated poly-(fluorenyl ether thioether ketone)	
Anion exchange membranes (AEM)		
Backbone	Anion exchange groups	**Advantage:** • Low V crossover **Challenges:** • Lack of long-term stability • Low ionic conductivity • Mechanical properties
polysulfone	pyridinium	
polyphenylene	quaternary ammonium	
poly(arylene ether ketone)	methylated imidazolium	
Porous membranes		
Microporous materials:	PIM-1 zeolites silica modified PAN/PTFE	**Advantage:** • Low V crossover **Challenges:** • unproved long-term stability • Low ionic conductivity
Charged micro/meso-porous (acid doped) membrane:	polybenzimidazole (PBI) Chloromethylated PSF	

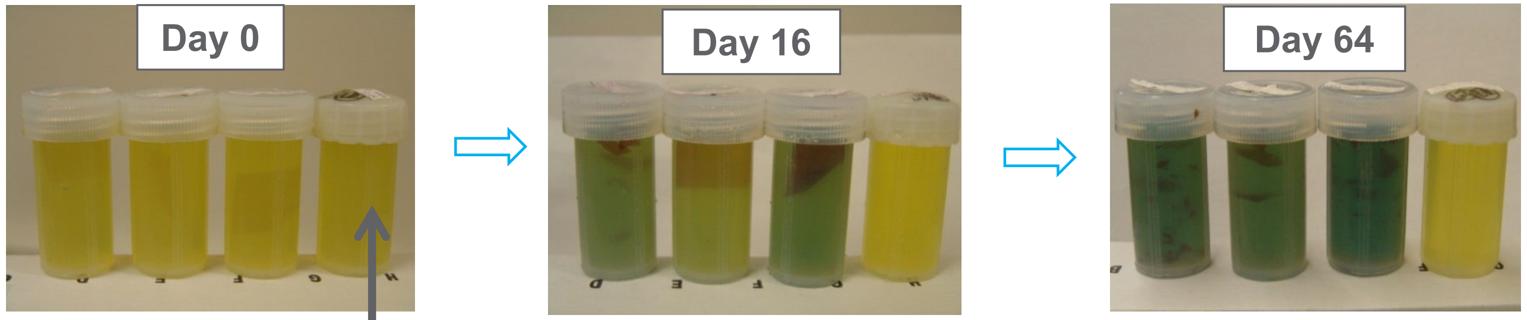
Wei et al. Adv. Energy Mater. 2013, 3, 1215
Schmidt-Rohr et al. Nat. Mater. 2008, 7, 75.

Major challenges for RFB membranes

Membranes for VRB systems

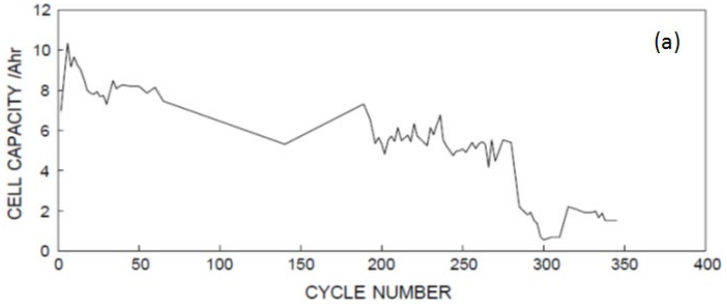
- Chemical stability towards VO_2^+ in highly acidic electrolyte

0.1M VO_2^+

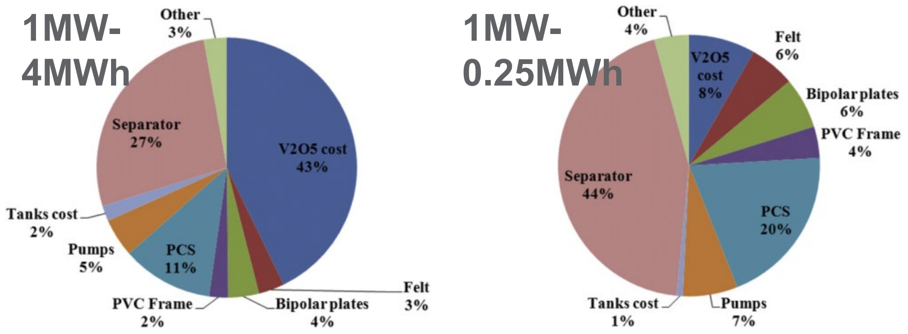


Nafion

- Limited selectivity



- High cost



Membranes for aqueous organic systems

- No available IEMs for neutral and alkaline organic electrolyte
- Diverse charge carriers (Na^+, K^+, OH^-)
- Less corrosiveness
- Less active materials cross-over
- Lower conductivity

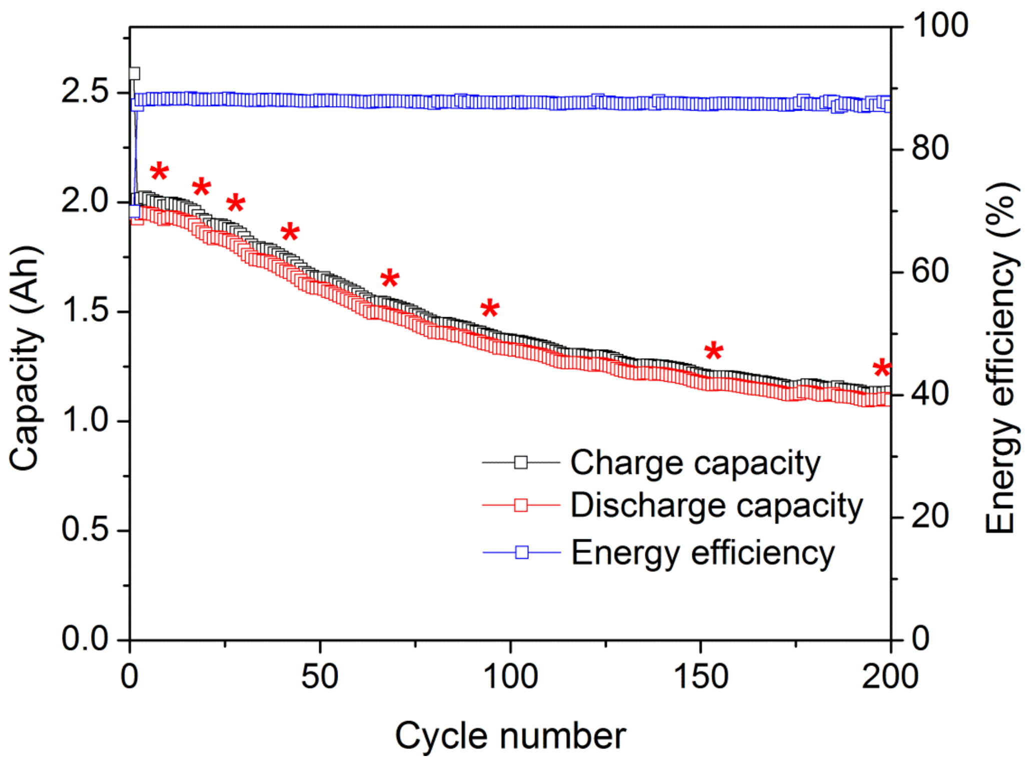
S. Kim, etx. Electrochemistry Communications 2010, 12, 1650.
C. Jia, J. Liu, C. Yan, Journal of Power Sources 2010, 195, 4380.
T. Sukkar, M. Skyllas-Kazacos, Journal of Applied Electrochemistry 2004, 34, 137.

Transport phenomenon - capacity decay in VRB

Capacity decay of RFB

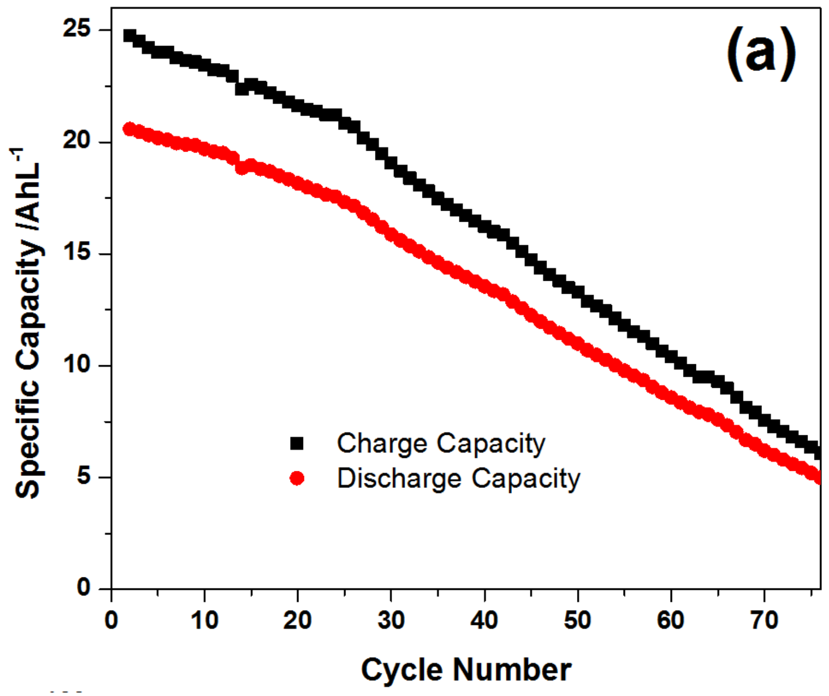
- ➢ Reduce energy output
- ➢ Increase possibility of gas evolution and precipitation
- ➢ Require routine maintenance

Capacity decay of Nafion-based VRB



ChemSusChem, **6**, 268, 2013.

Capacity decay of separator-based VRB

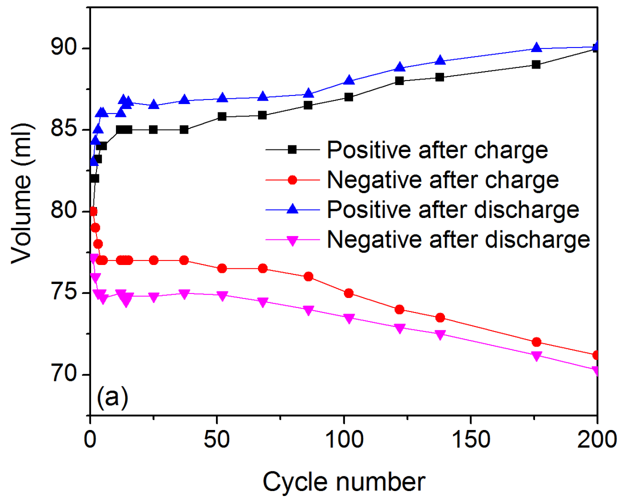


ChemSusChem, DOI: 10.1002/cssc.201300706

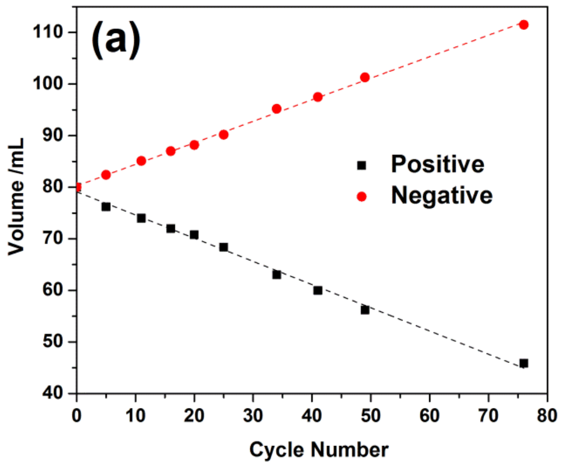
Transport phenomenon - Imbalance electrolyte transfer

Nafion based VRB

Separator based VRB

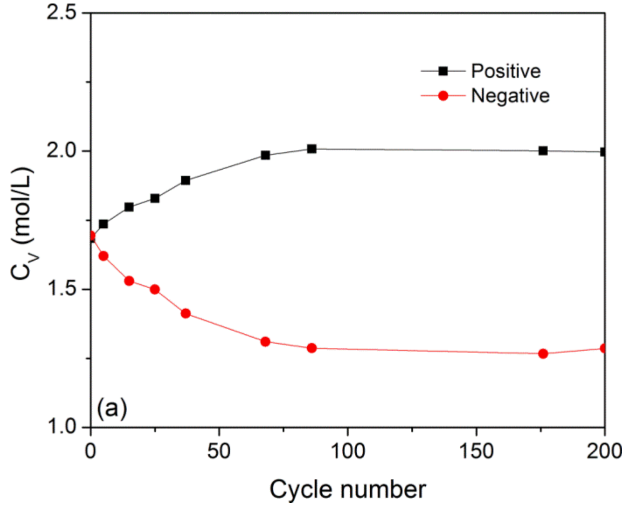


Electrolyte volume

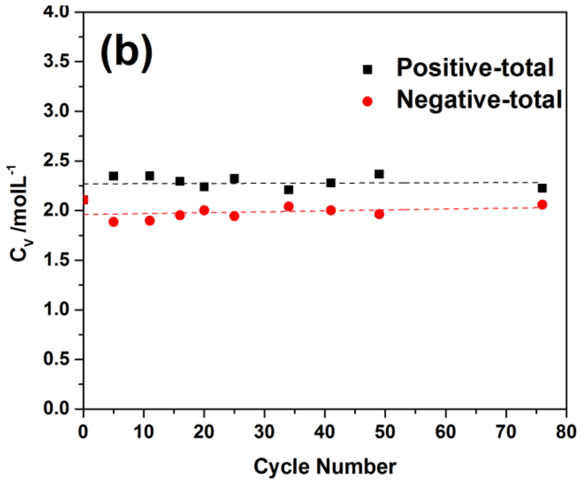


Negative limiting

Positive limiting

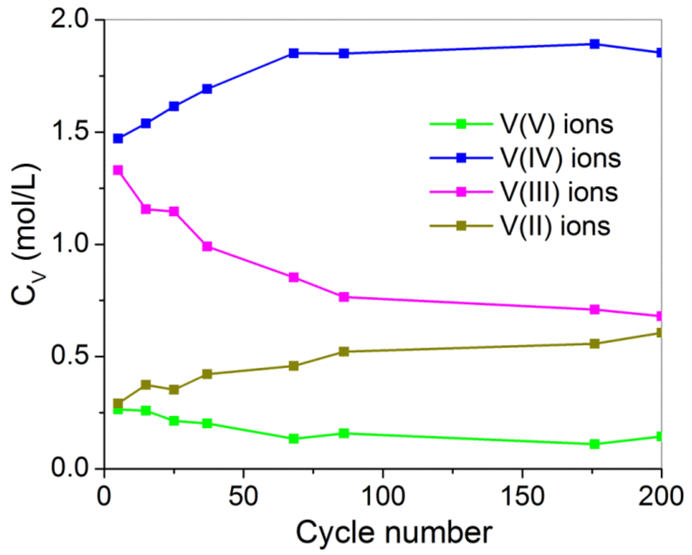


Total V concentration

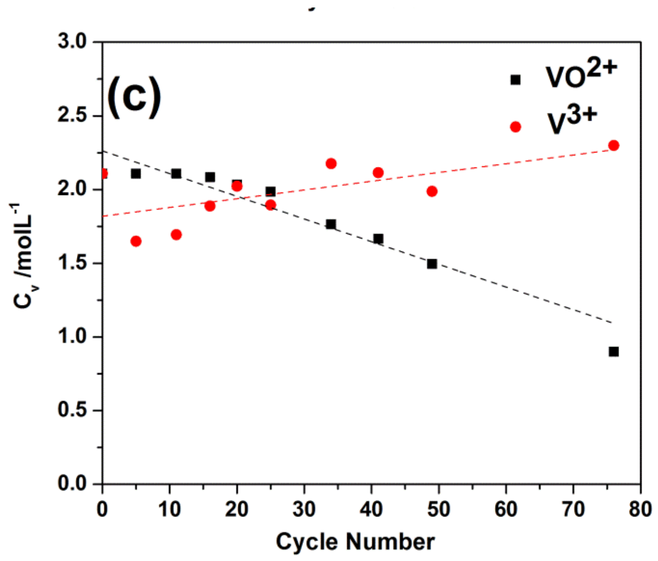


Transport phenomenon - Asymmetrical valence change

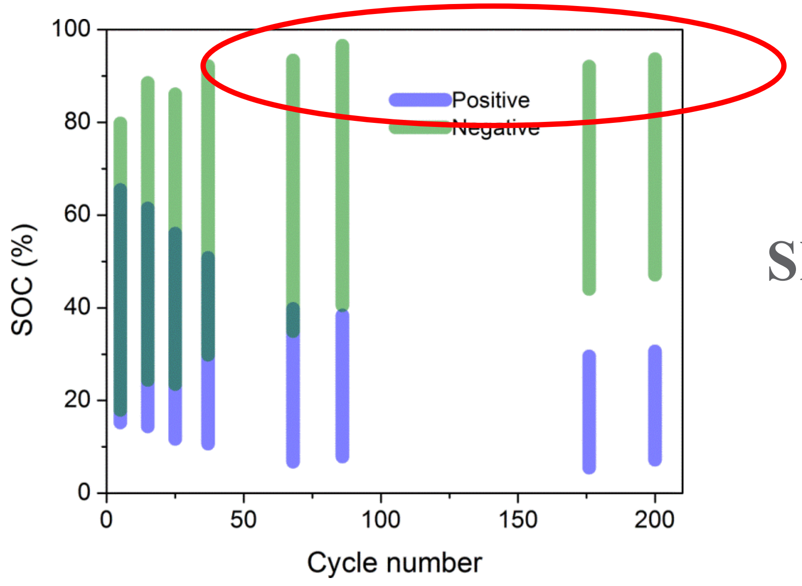
Nafion based VRB



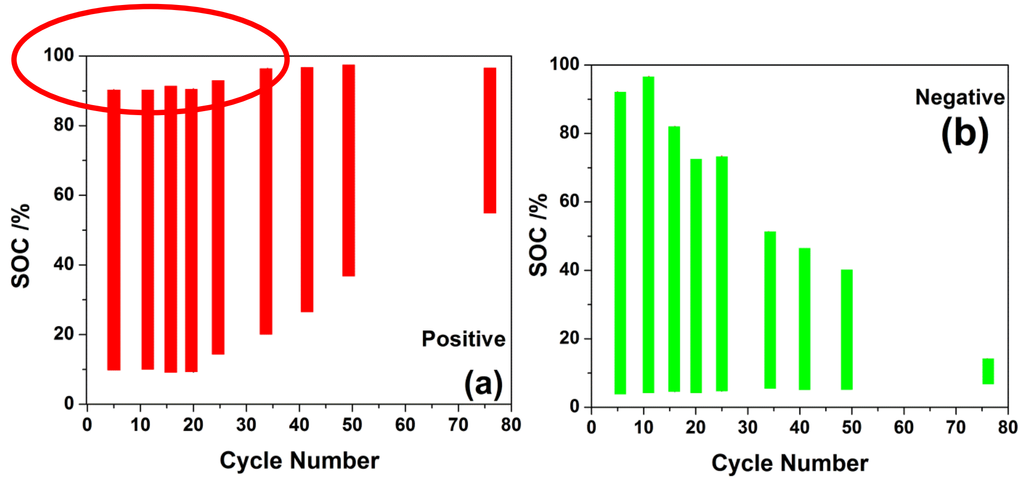
Separator based VRB



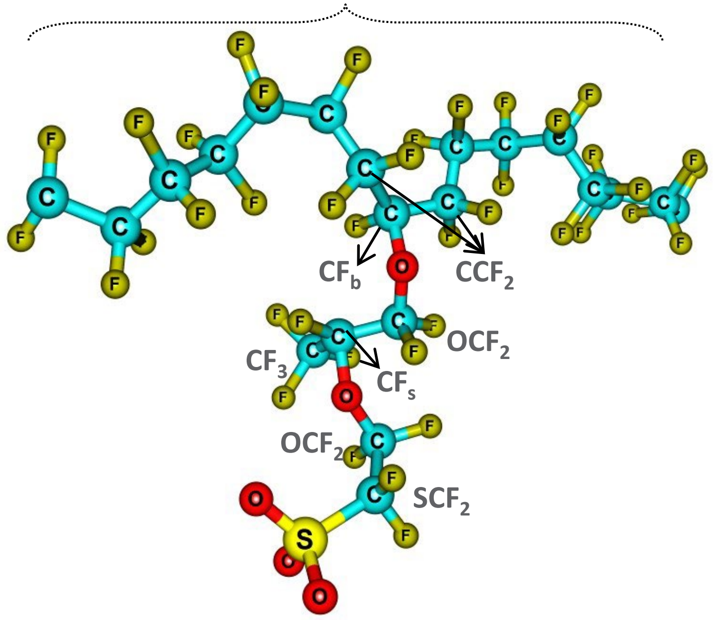
Concentration of V^{n+}



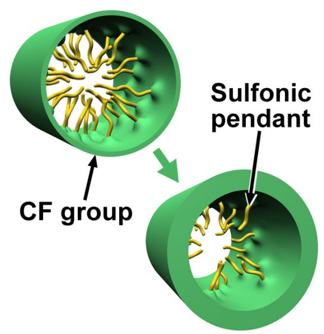
Shifting of SOC

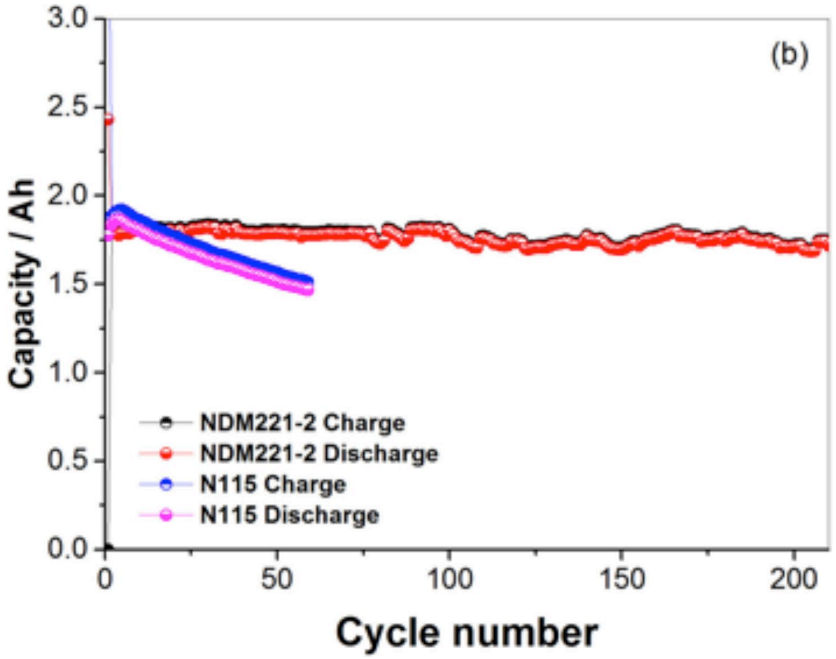


Optimize of Nafion membrane



- Equivalent weight (EW) is the weight of polymer that contains one mole of charge.
- As EW increased, crystallinity increased. Change in the EW value changes the structure of the Nafion membrane.
- Membranes with different EW values are prepared, 1000 and 1500.



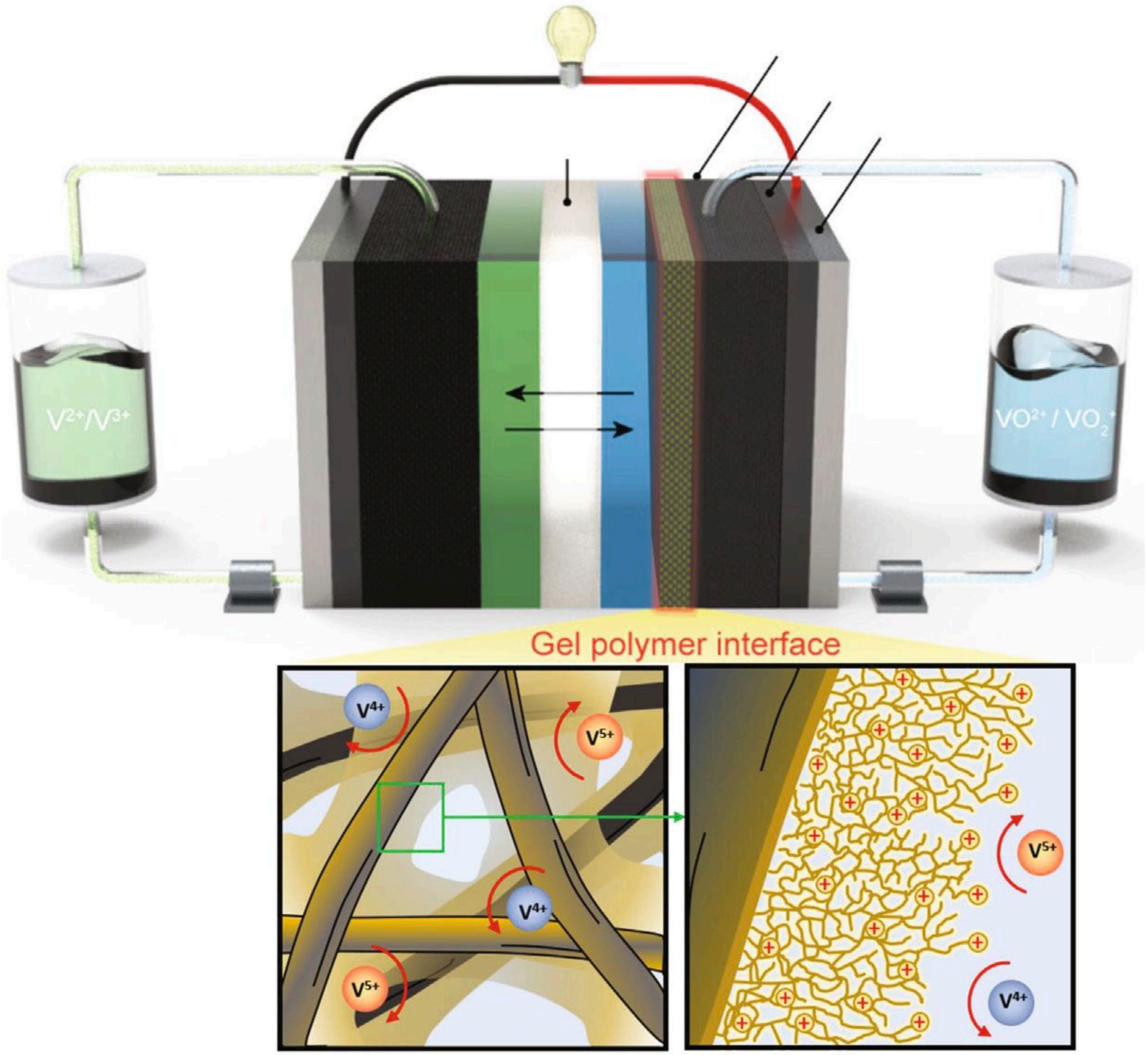


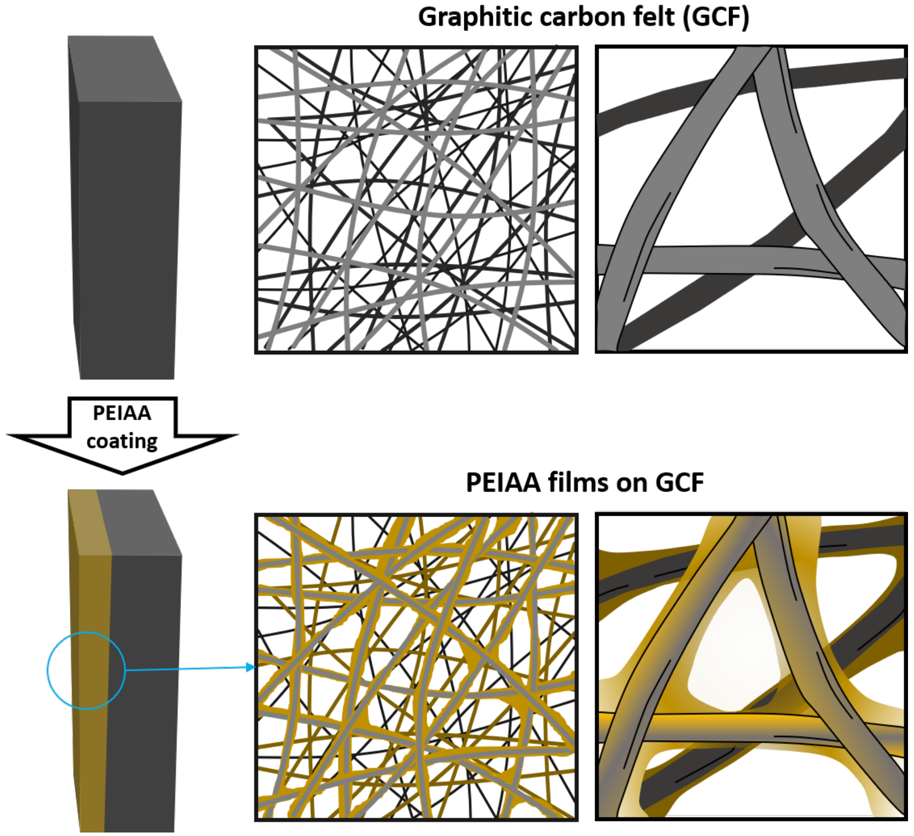
Membrane	EW	Thickness (μm)	Water uptake (%)	Conductivity (mS cm^{-1})	Area resistance (mΩ cm2)	Diffusion Coefficient of VO^{2+} (*10^{-6} cm^2 min^{-1})	VO^{2+} ion flux (*10^{-7} mol cm^{-2} min^{-1})	Selectivity Between H^+ and VO^{2+}
NDM221-2	1500	31	3.2	16	157	0.17	0.53	98
N115	1000	135	17.8	77.9	179.1	1.2	0.89	64.9

M. Vijayakumar, etc. ACS Appl. Mater. Interfaces 2016, 8, 34327−34334

Solving capacity decay without membrane modification

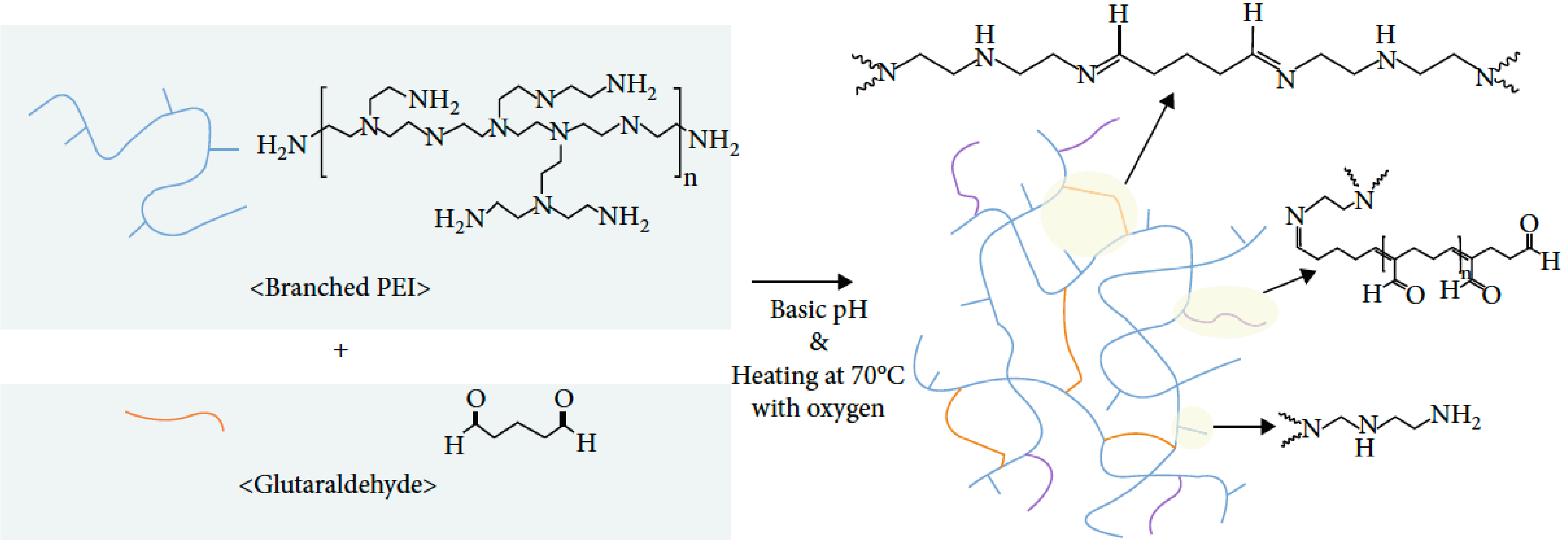
Gel Polymer Interface (GPI)

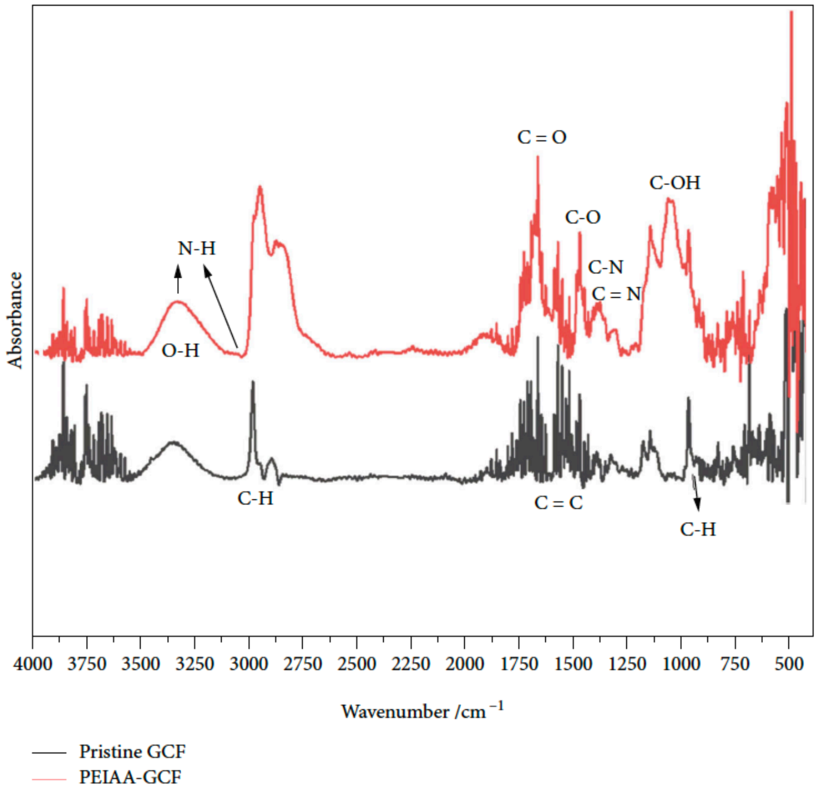




Hyung-Seok Lim, etc. Energy Material Advances, Volume 2022, Article ID 9863679

Crosslinked Polyethyleneimine GPI Design and Synthesis

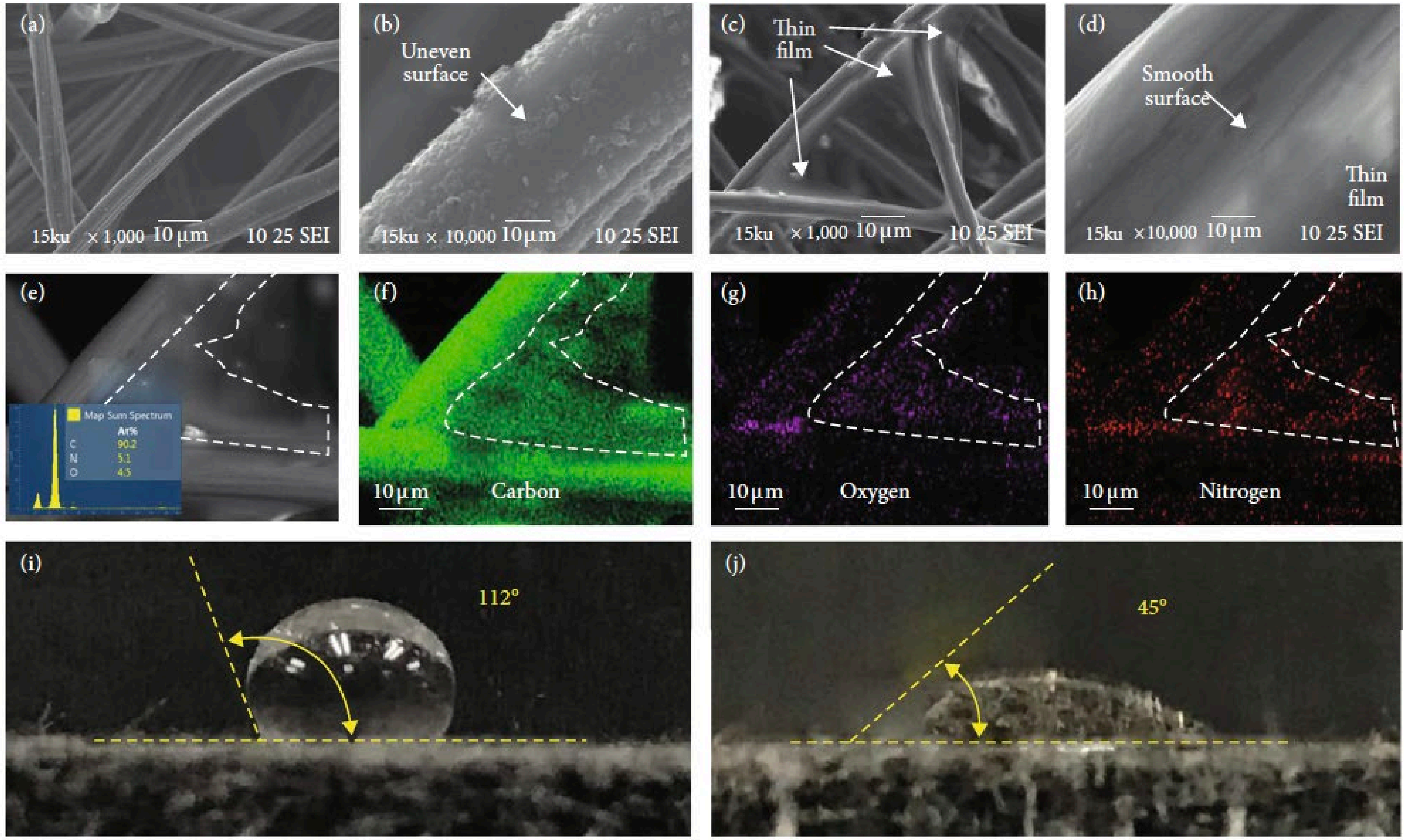




Chemical structures of polyethyleneimine and Glutaraldehyde and their chemical reaction to form crosslinked regions and amino and carboxylic acid groups.

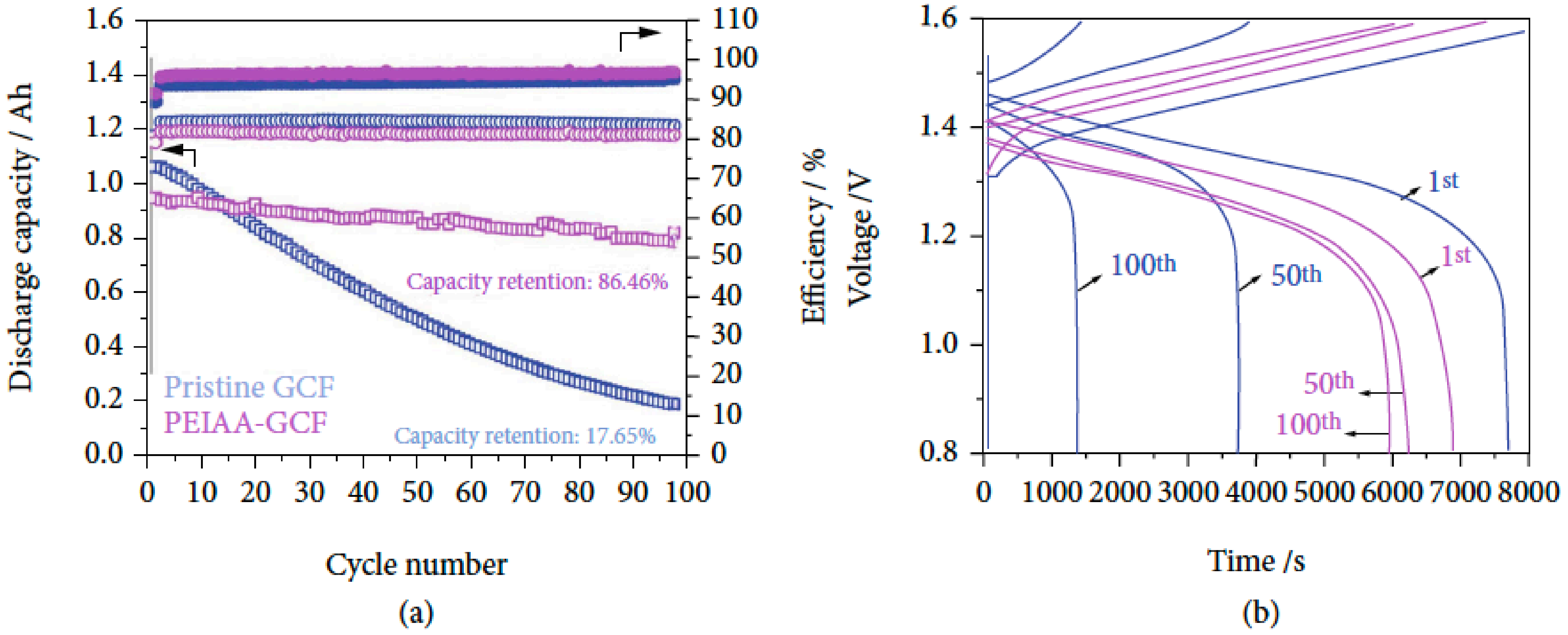
FTIR spectra of (black) pristine GCF and (red) PEIAA-GCF samples.

Characterization of the Crosslinked Polyethyleneimine GPI



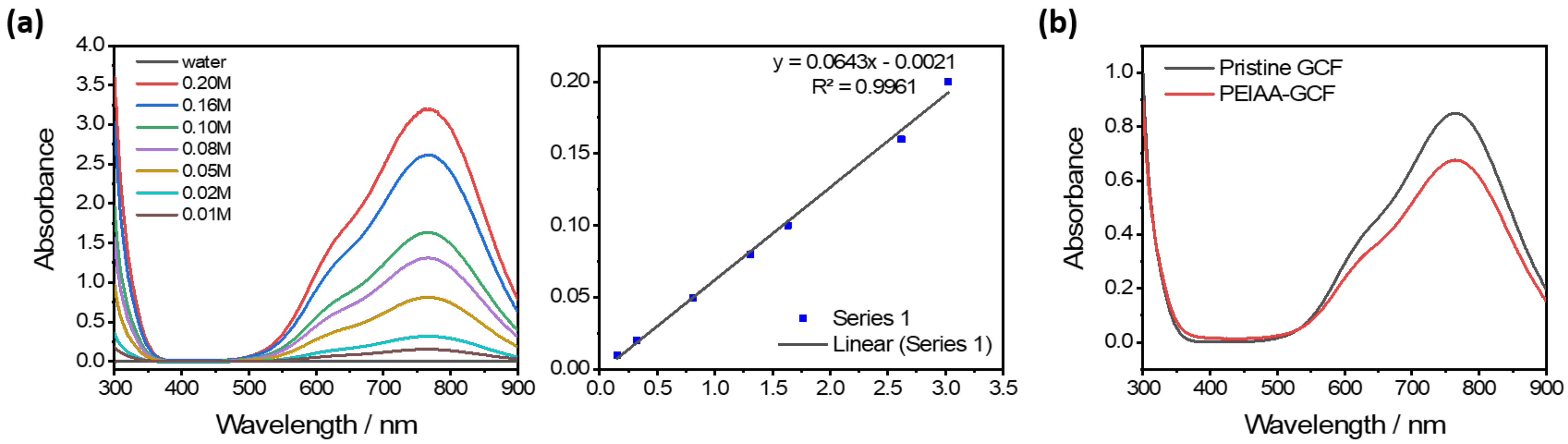
SEM images of (a, b) pristine GCF and (c, d) PEIAA-GCF samples with different magnifications (1,000x and 10,000x). SEM-EDX, (e) spectrum and element maps ((f) carbon, (g) oxygen, and (h) nitrogen) of a part of PEIAA-GCF sample. Contact angles of (i) the pristine GCF and (j) the PEIAA-GCF samples.

Flow Battery Test Validation



(a, empty square) Discharge capacity, (a, solid circle) Coulombic efficiency, and (a, empty circle) energy efficiency; (b) voltage time profiles of 1st, 50th, and 100th cycles of cells with (blue) pristine GCF and (pink) PEIAA-GCF electrodes under constant current charge at $50 mAcm^{-2}$.

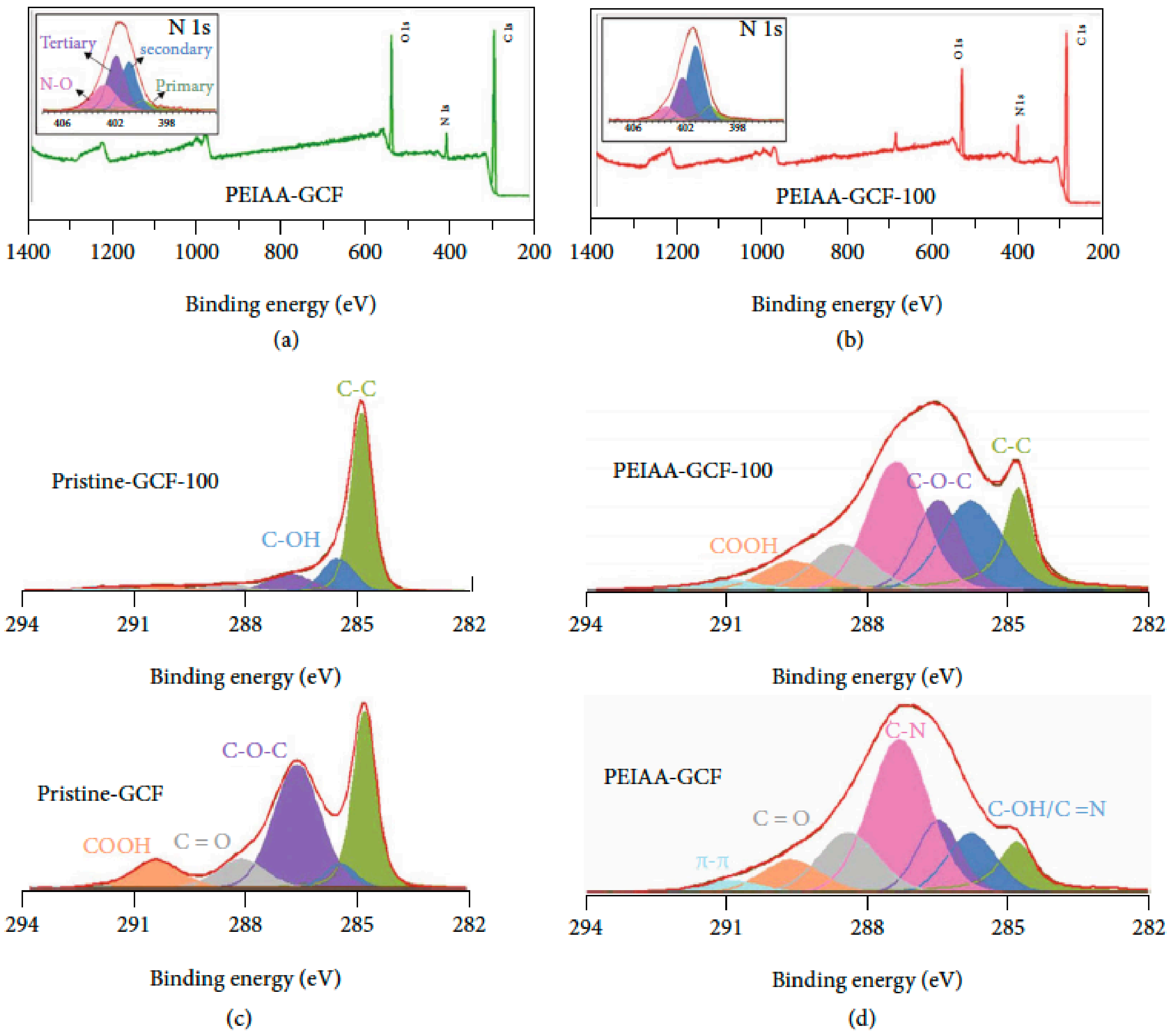
Mechanistic study – Reducing V(IV) ion crossover



~25% less V(IV) crossover

(a) UV-Vis spectra of the $V(IV)OSO_4$ solutions ranging from 0.01 M to 0.2 M with a standard calibration curve and (b) UV-Vis spectra of the 3.5M sulfuric acid solutions with (black) pristine GCF or (red) PEIAA-GCF electrode after 5 days with a flow rate of 30 mL min^{-1} for crossover test.

Stability of the Crosslinked Polyethyleneimine GPI



Wide scan XPS and inserted N 1 s spectra of PEIAA-GCF electrodes (a) before and (b) after 100 cycles under constant current charge at 50mAcm^{-2}. High-resolution XPS C 1 s spectra of (c) pristine GCF and (d) PEIAA-GCF electrodes before and after 100 cycles.

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Summary

- We demonstrate a new gel polymer interface (GPI) consisting of crosslinked polyethyleneimine with a large amount of amino and carboxylic acid groups introduced between the positive electrode and the membrane.
- The GPI functions as a key component to prevent vanadium ions from crossing the membrane, thus supporting stable long-term cycling.

Acknowledgement

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- Pacific Northwest National Laboratory is a multi-program national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy.