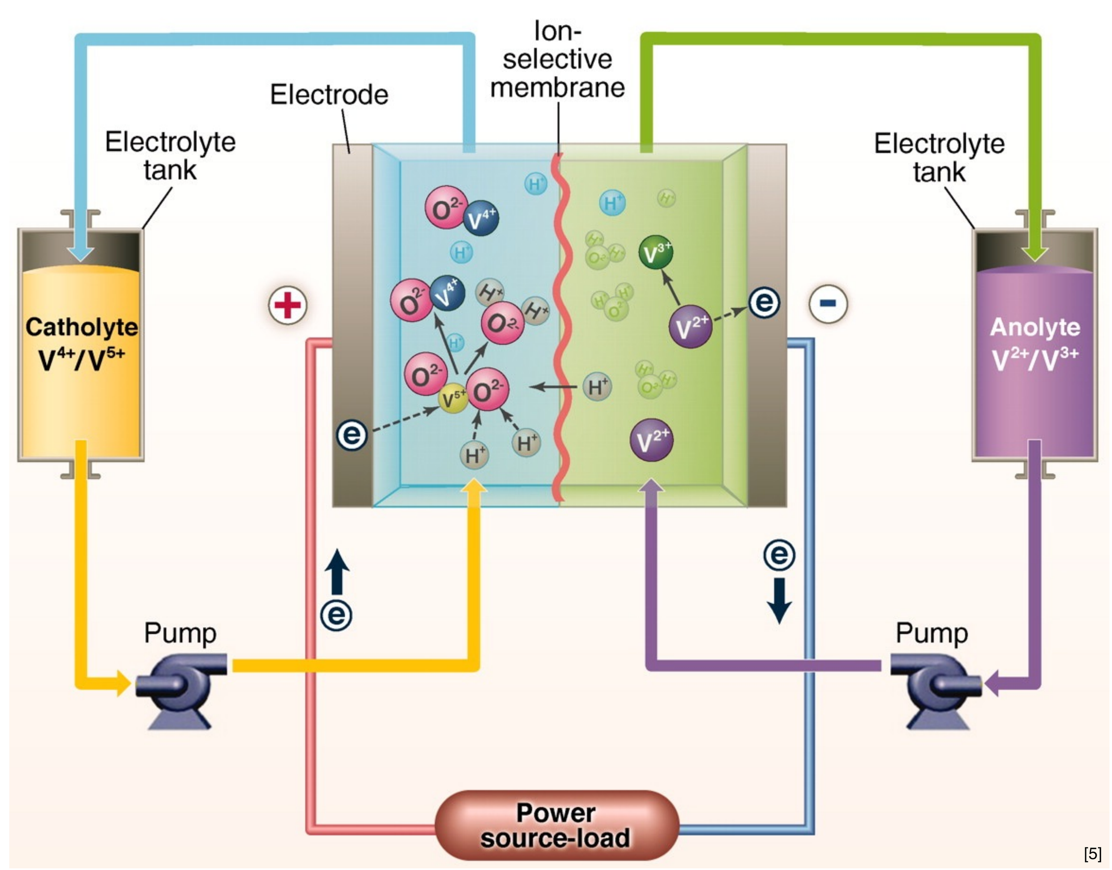
Combining cationic and anionic exchange membranes to improve the efficiency of vanadium redox flow batteries

Cameron Quinlan, Rodney D. L. Smith

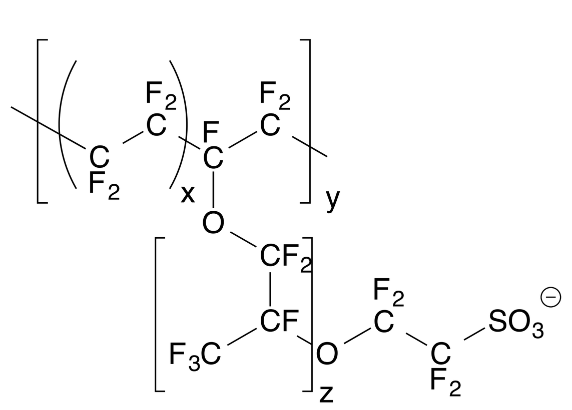
Undergraduate Research Opportunities: Research Experience Program (www.uroubc.ca)
Faculty of Science, University of British Columbia

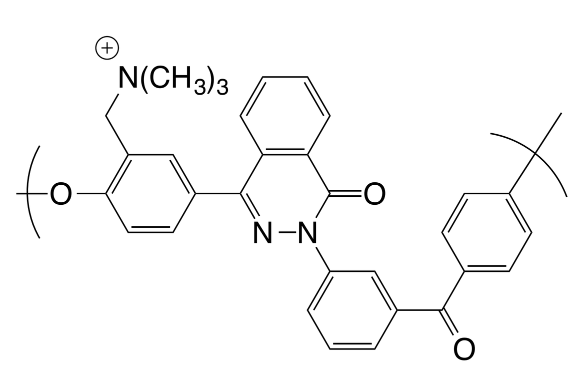
Overview

The all vanadium redox flow battery (VRFB), shown below, is a promising technology for large-scale renewable energy storage. Although numerous VRFB pilot projects are operational at sites around the world, there remains room for significant improvement in the energy efficiency (EE) of these batteries. Ion-selective membranes are a critical component within this technology that plays two critical roles: they keep the redox active species separated from one another, thereby improving the Coulombic efficiency (CE), while allowing the transport of non-redox active supporting electrolyte ions, reducing the cell resistance and enhancing the voltage efficiency (VE).



Ion-selective membranes can be separated into two categories: cationic exchange membranes (CEMs) and anion exchange membranes (AEMs). The negative charge inherent in CEMs make them excellent cation conductors. Their ability to rapidly transport H^+ imparts a low cell resistance and therefore a high voltage efficiency (VE). However, the anionic charge on CEMs also enables transport of positively charged vanadium ions between the anolyte and catholyte, lowering the CE. Alternatively, the positive charge present on AEMs such as quaternized poly(phthalazinone)ether ketones (QAPPEK) blocks transport of vanadium ions, increasing CE, but suffers from poor transport of supporting electrolyte, decreasing VE. This research project will determine whether the combination of AEMs and CEMs in a single membrane will produce an ion-selective membrane with improved anion CE and VE.





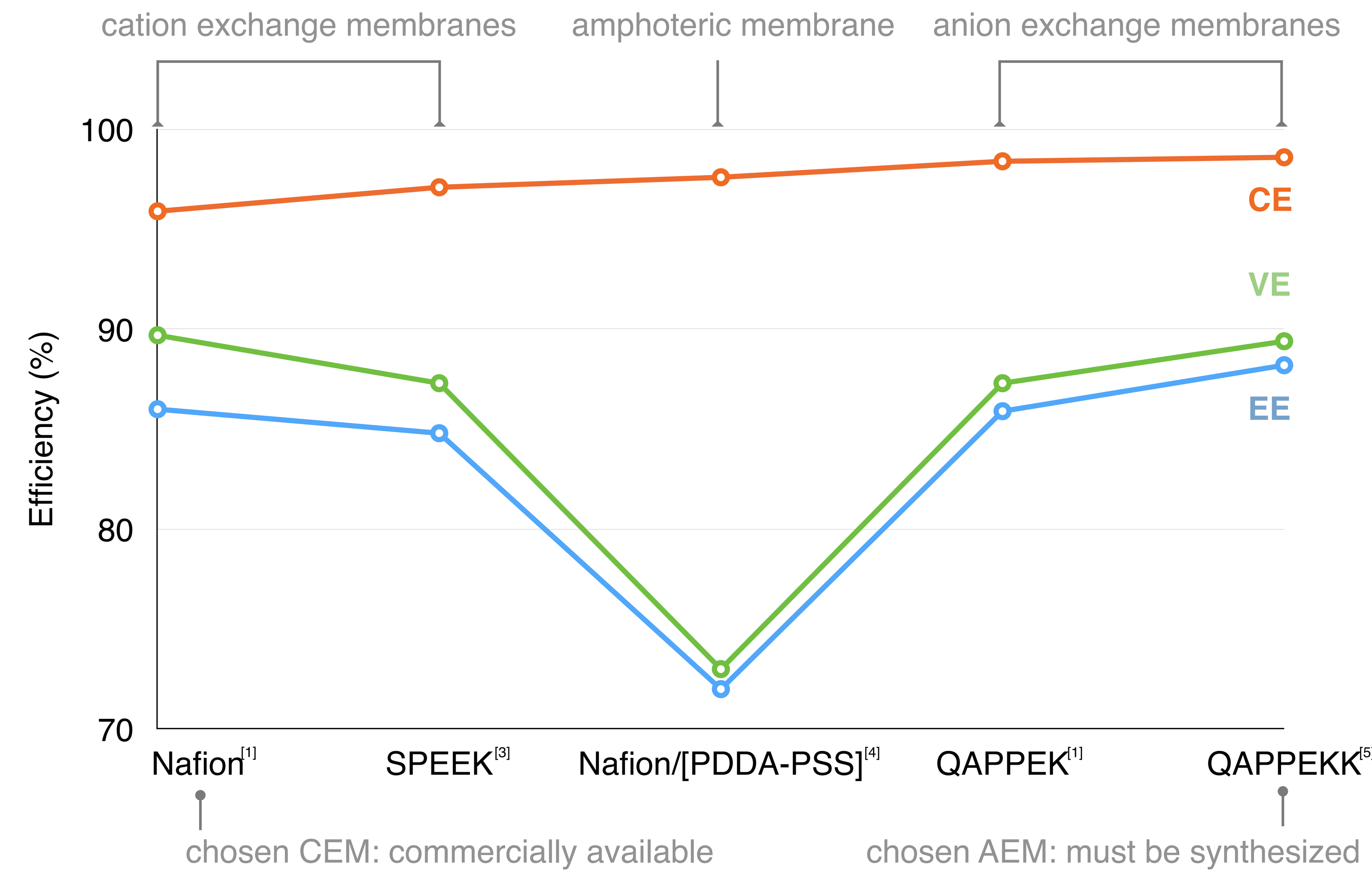
Nafion[1]	
CE (%)	95.9
VE (%)	89.7
EE (%)	86.0
Thickness (μm)	175

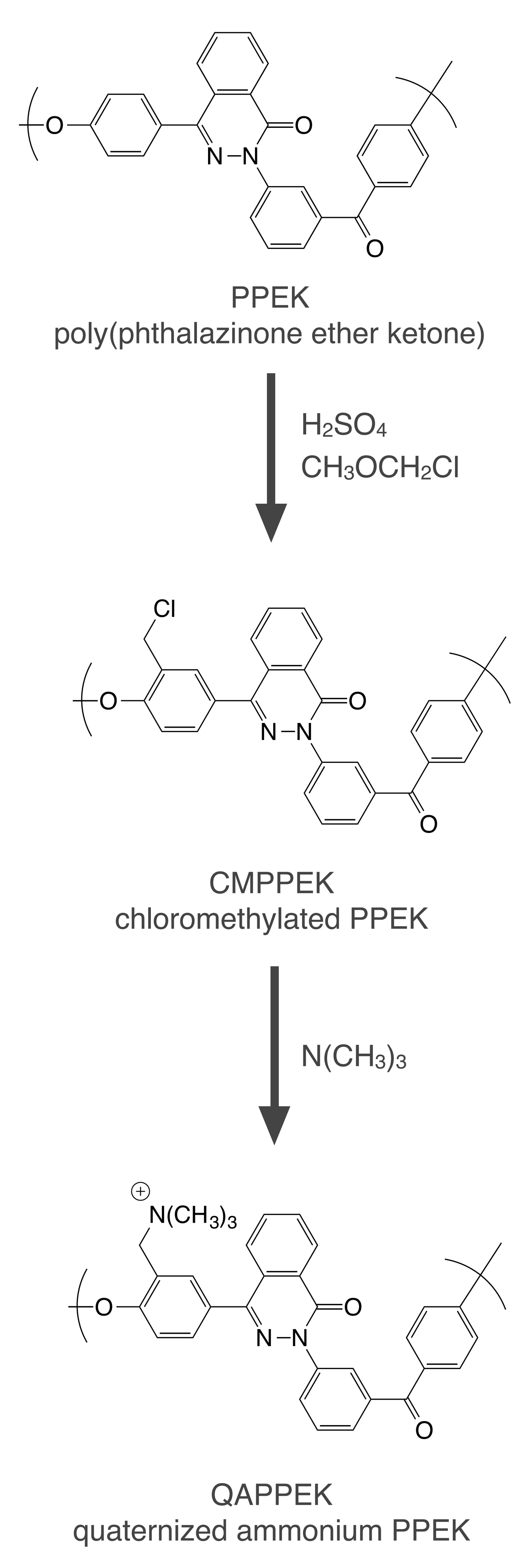
- Commercially available
- Chemically stable
- High voltage efficiency
- High cost

QAPPEK[1]	
CE (%)	98.4
VE (%)	87.3
EE (%)	85.9
Thickness (μm)	40

- Not commercially available
- Chemically stability
- High coulombic efficiency
- Easy to synthesize relative to other AEMs

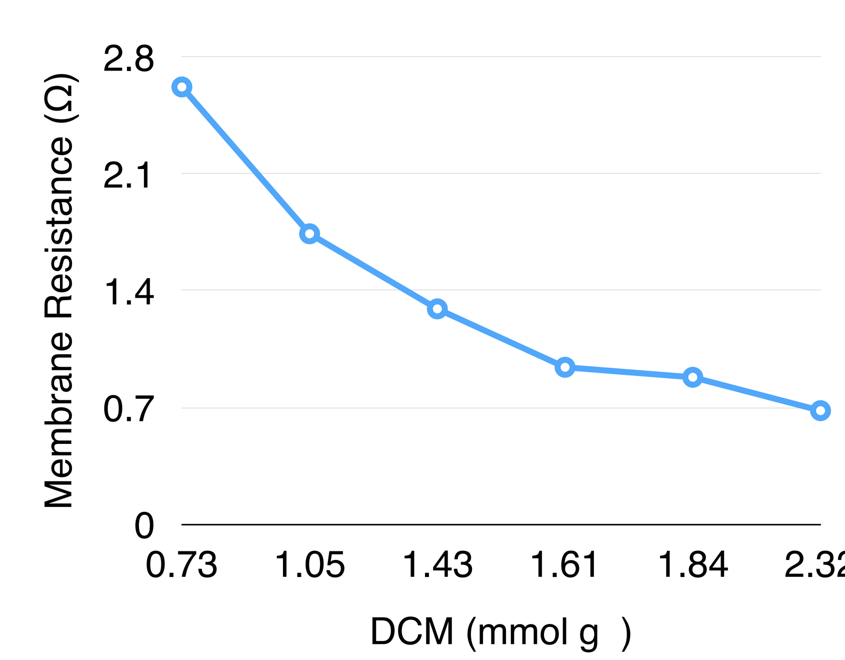
Membrane Selection & Preparation



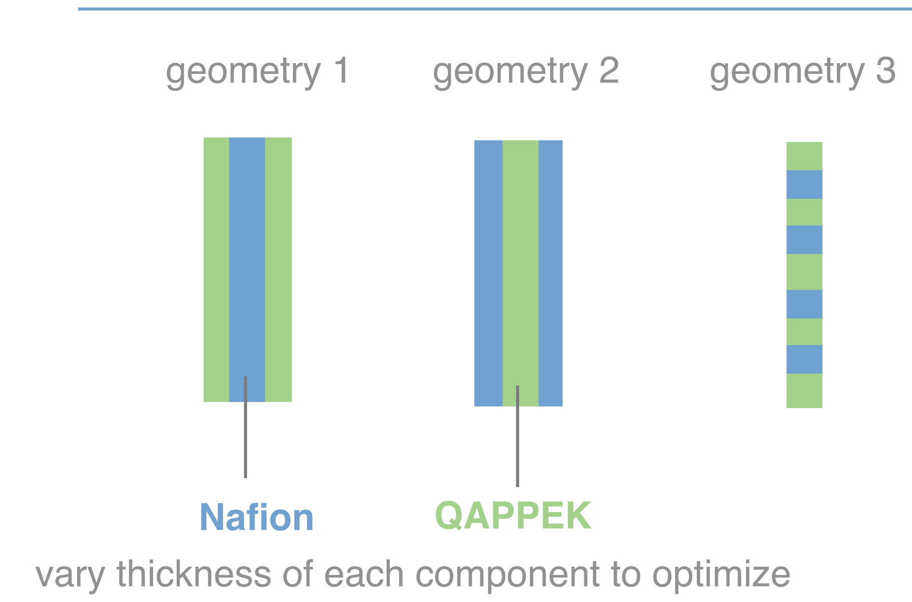


AEM Synthesis

- Greater degree of chloromethylation (DCM) provides more sites to install quaternized ammonium groups
- More ammonium groups yield improved ionic conductivity
- Titrate CMPPEK with potassium thiocyanate (KSCN) to determine DCM ($NH_4(Fe(SO_4)_2)$ as indicator):[1]



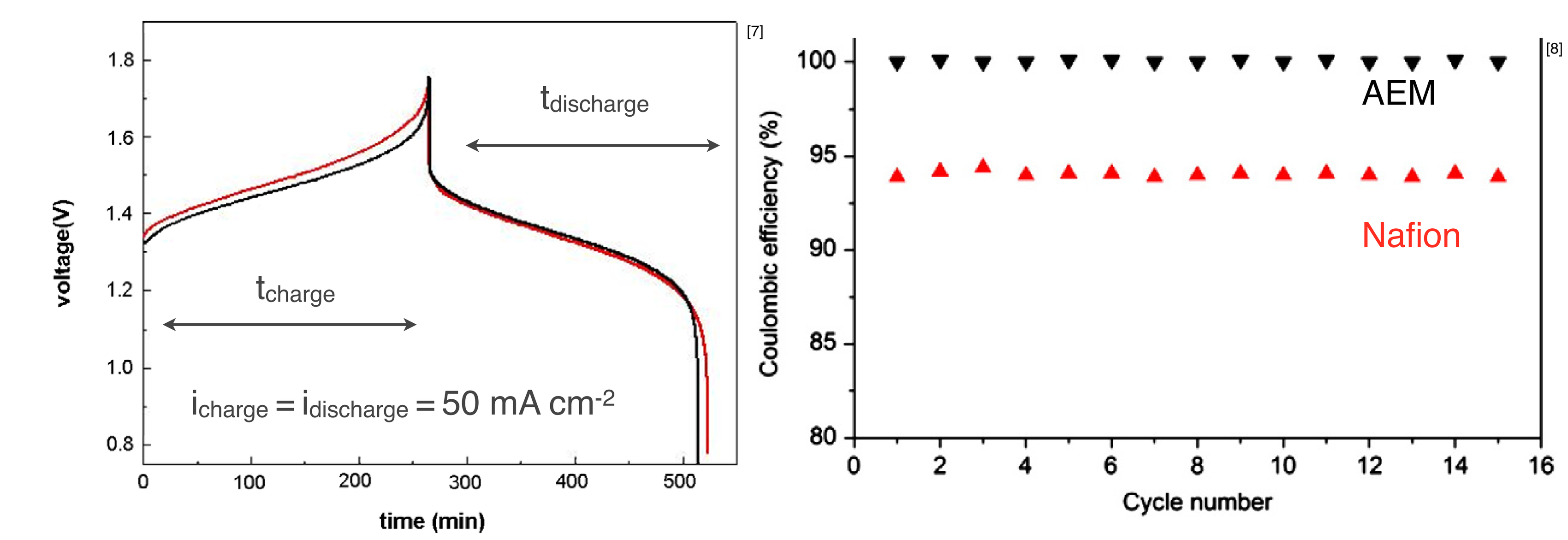
Composite Membranes



Anticipated Results

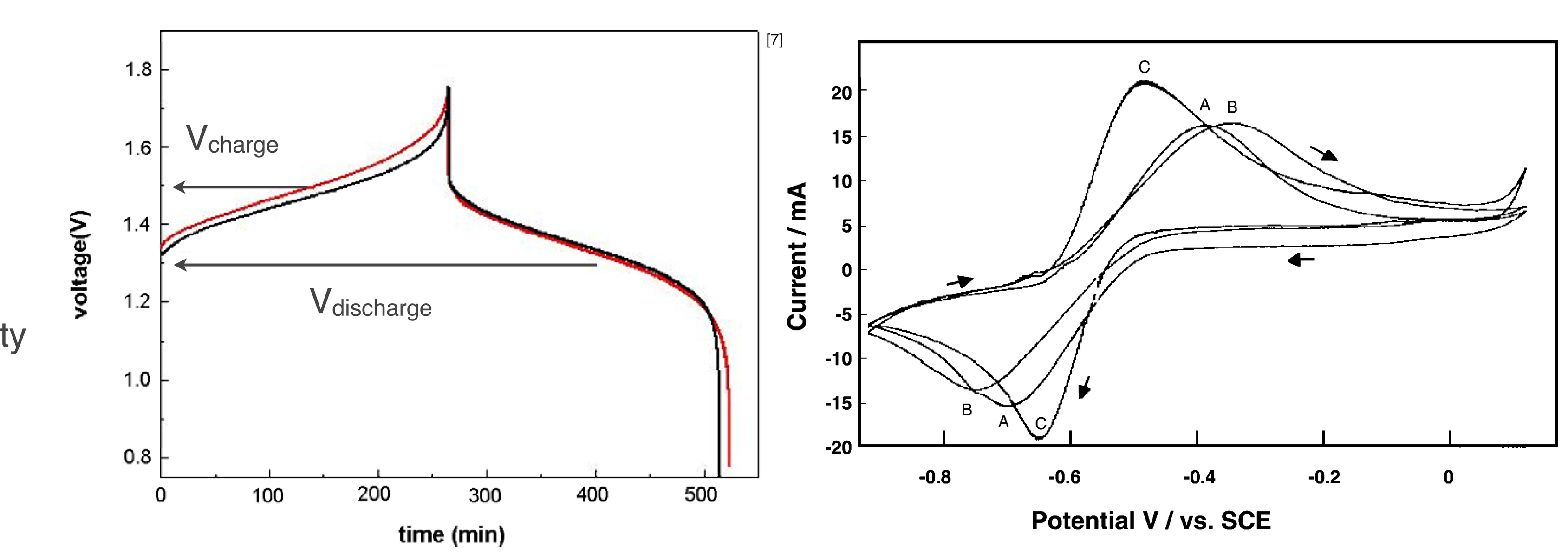
Coulombic Efficiency

$$CE = \frac{Q_{discharge}}{Q_{charge}} = \frac{(i_{discharge})(t_{discharge})}{(i_{charge})(t_{charge})}$$



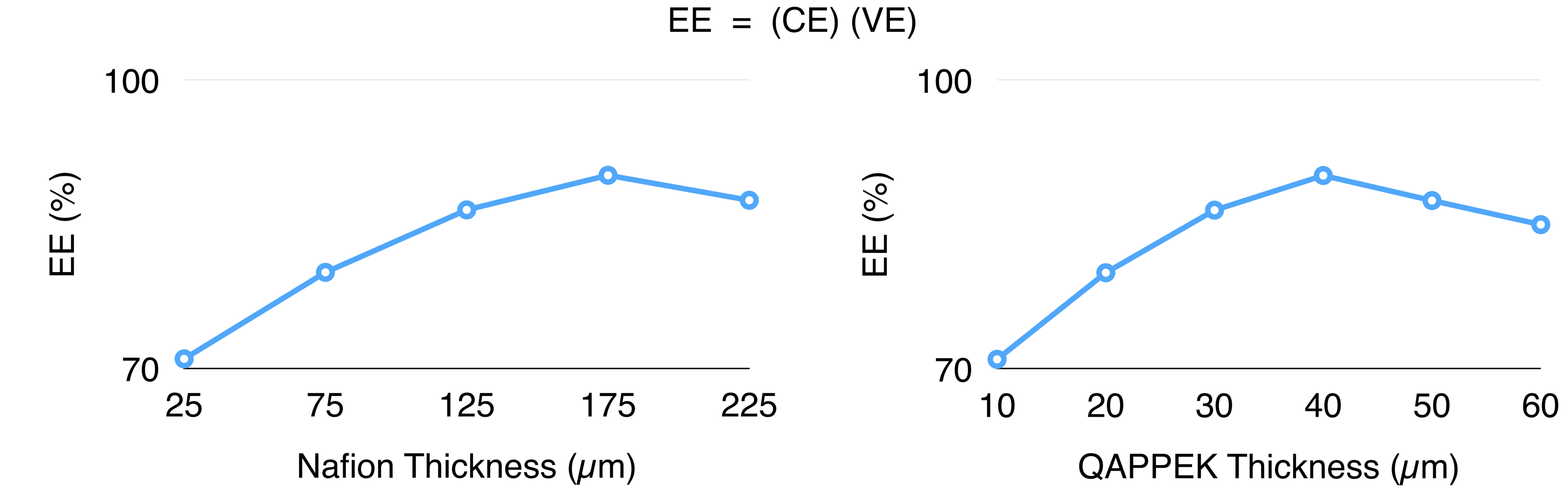
Voltage Efficiency

$$VE = \frac{(V_{discharge})}{(V_{charge})}$$



Energy Efficiency

$$EE = (CE)\,(VE)$$



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Acknowledgements

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