Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

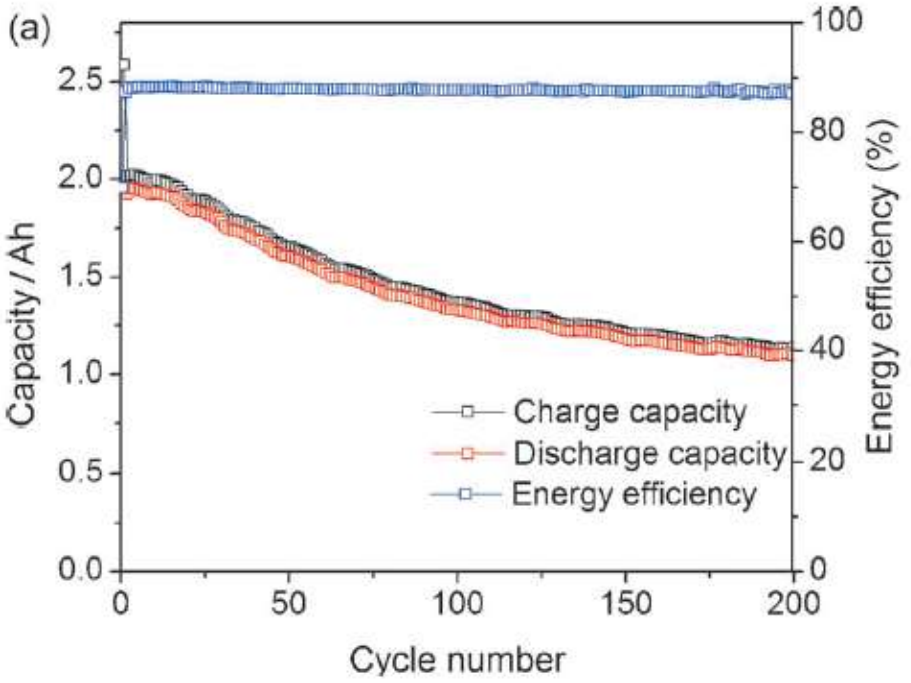
In-situ reliability studies on vanadium flow batteries

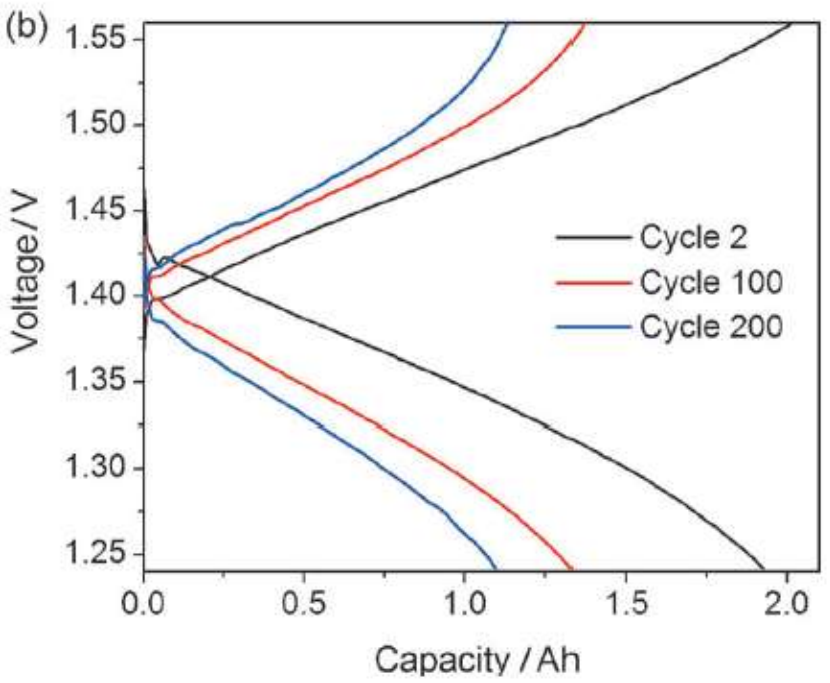
Bin Li, David Reed and Vincent Sprenkle

Energy Storage Systems 2019 Safety & Reliability Forum
Albuquerque NM

U.S. DEPARTMENT OF ENERGY

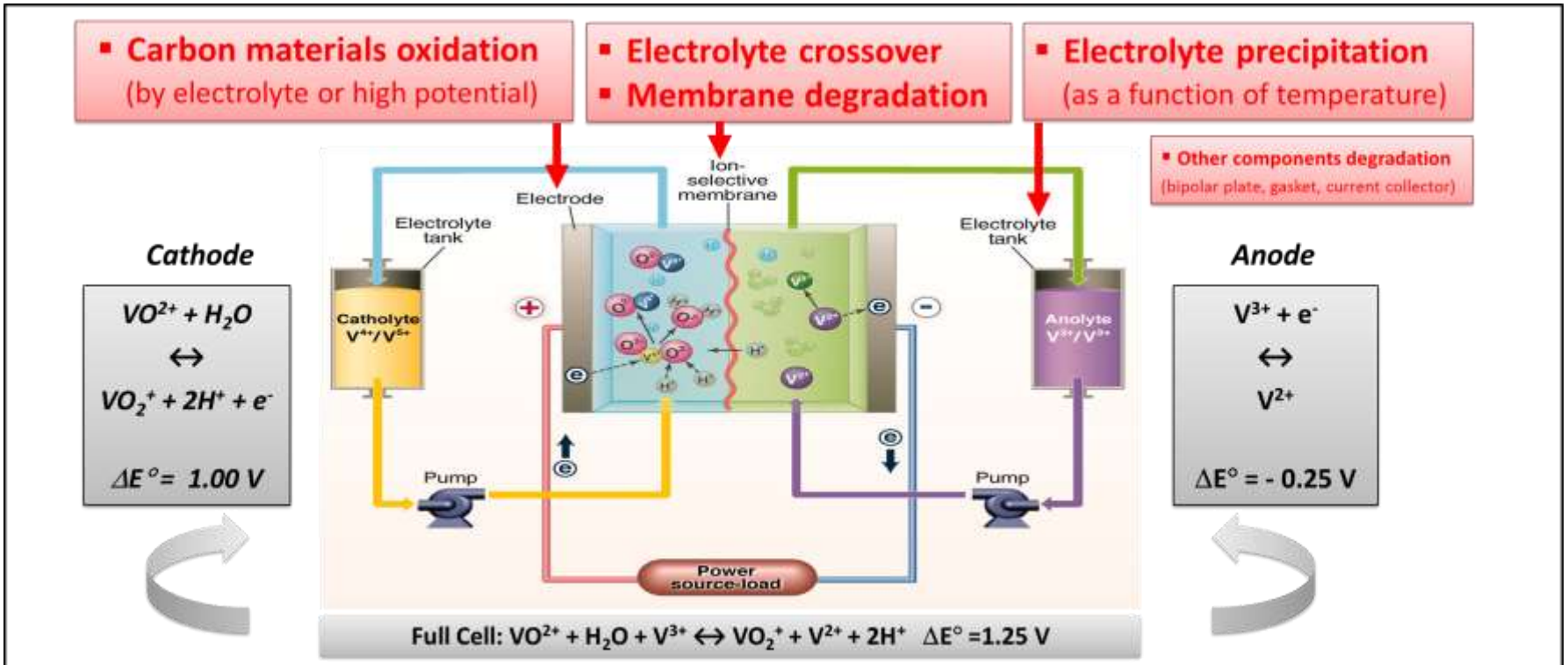
VRB Decay





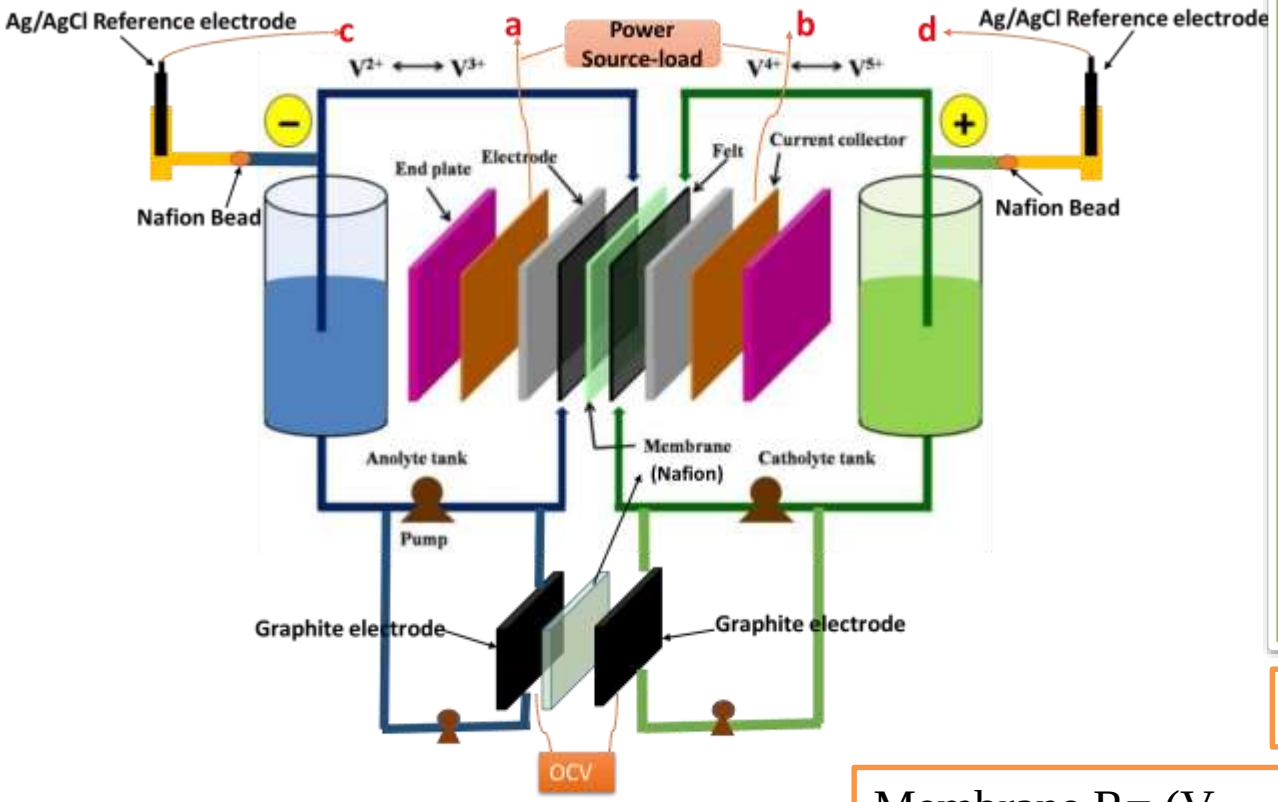
ChemSusChem, 2013, 6, 268

VRB decay mechanisms



Vanadium Redox Flow Battery (VRFB) Degradation Mechanisms

In-situ Set Up



In-situ measurements:

- $V_{Full\ cell\ (b\ vs.\ a)}$
- $V_{cathode\ vs.\ Ref(+)\ (b\ vs.\ d)}$
- $V_{anode\ vs.\ Ref(-)\ (a\ vs.\ c)}$
- $V_{cathode\ vs.\ Ref(-)\ (b\ vs.\ c)}$
- OCV
- Polarization curves (such as full cell (b vs. a), cathode (b vs. d) and anode (a vs. c))
- Ac impedances

$$\text{Full Cell } R = (OCV - V_{output})/I$$

$$\text{Membrane } R = (V_{cathode\ vs.\ Ref\ (+)} - V_{cathode\ vs.\ Ref\ (-)})/I$$

Baseline:

Charge/discharge voltage: 1.6-0.8V; Flow rate: 80 ml/min; RT

Stressor Testing:

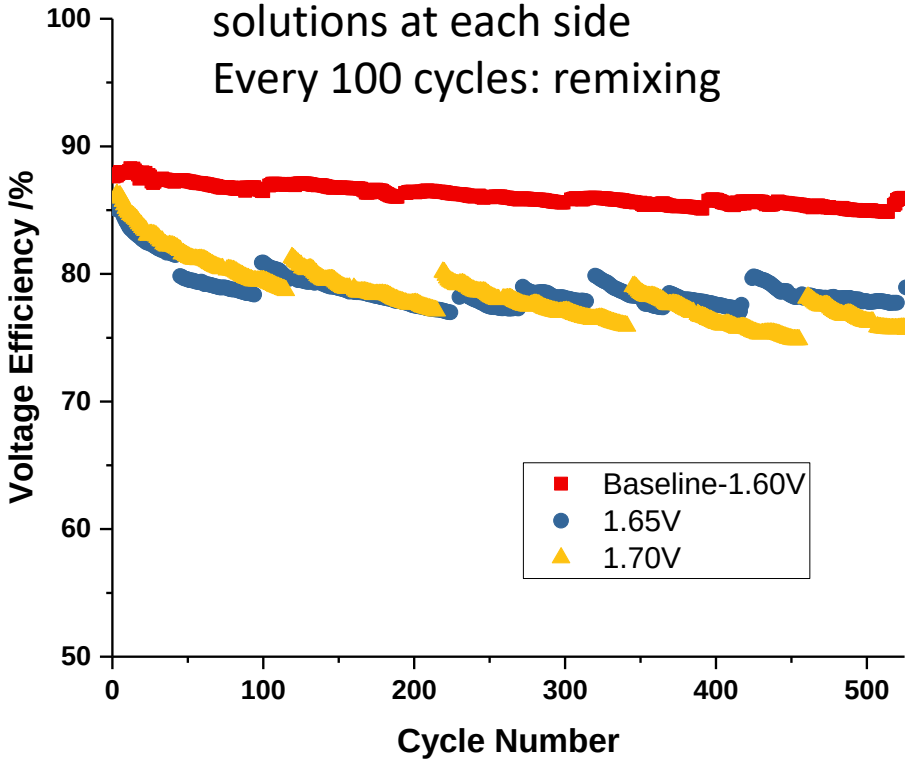
PNNL: *High Voltage; Catholyte Starvation; Anolyte Starvation*;

NRC: *High Current Density; Temperature; Depth of discharge*

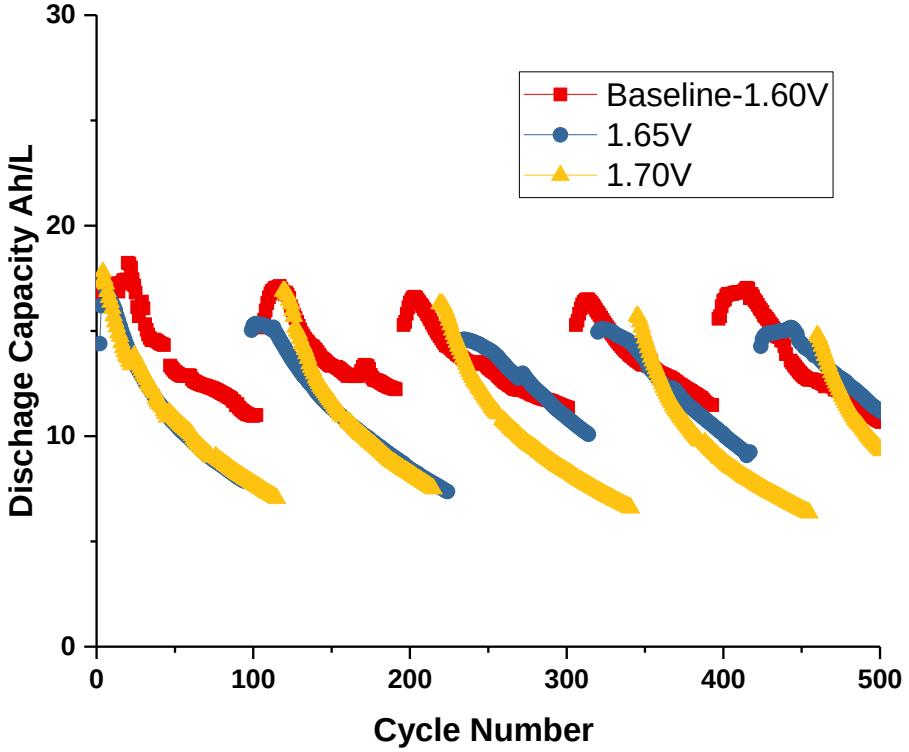
Stressor: High voltage

Upper voltage: 1.60 V; 1.65 V; 1.70 V

Every 50 cycles: taking out 1 ml solutions at each side
Every 100 cycles: remixing

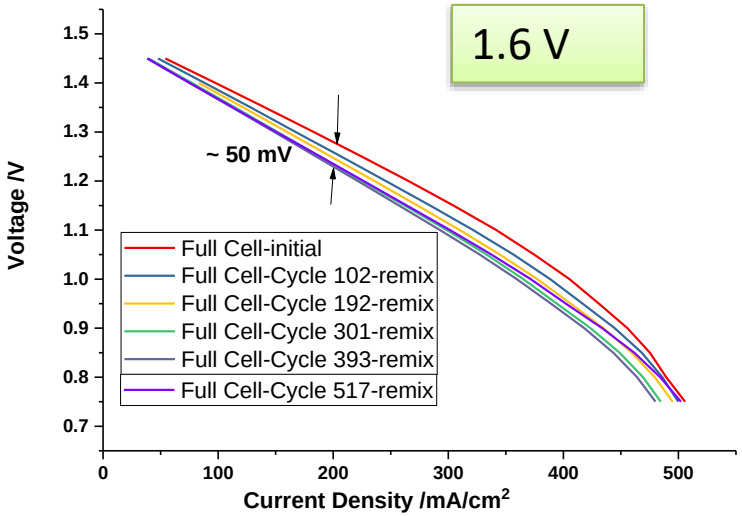


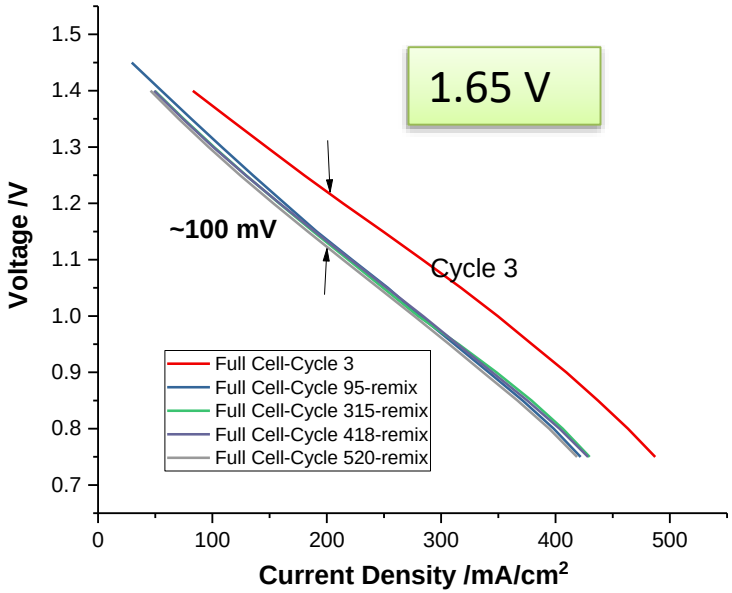
Membrane: Nafion 212
Electrolyte: 0.8 M V^{3+}+ 0.8M V^{4+} + 4M H_2SO_4 + 0.1M H_3PO_4

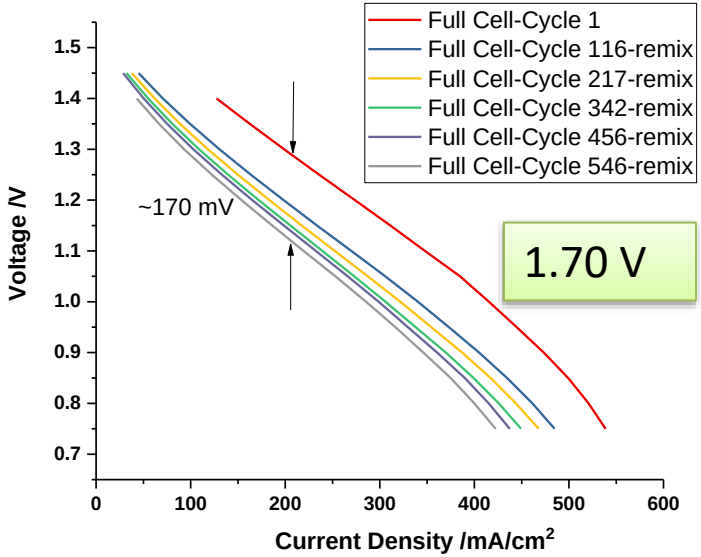


Higher voltage leads to decay more significantly

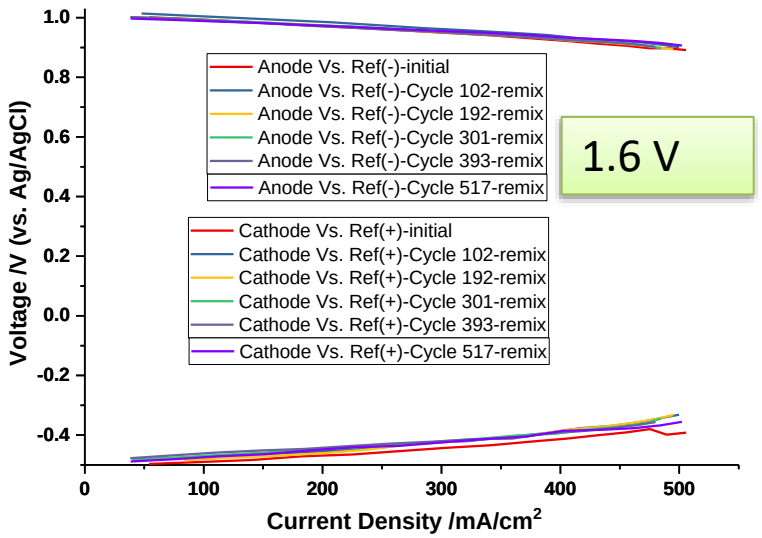
Polarization Curves-Full Cell for remixed solutions

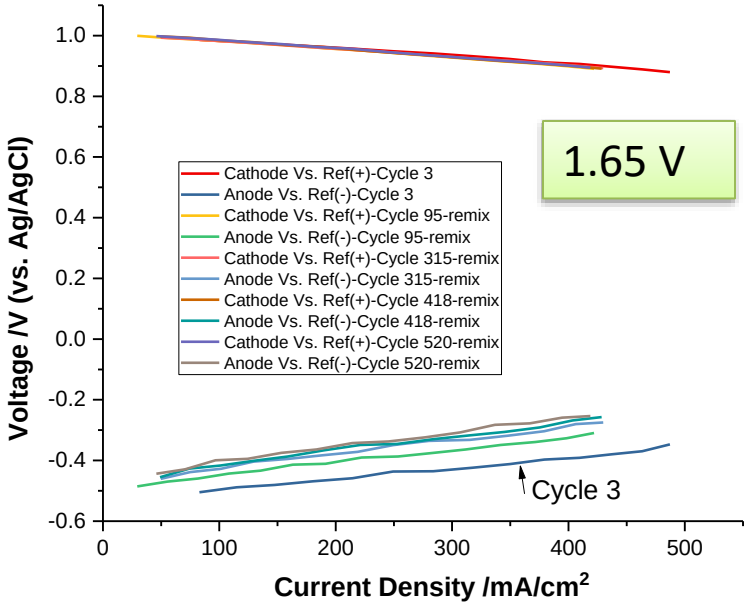


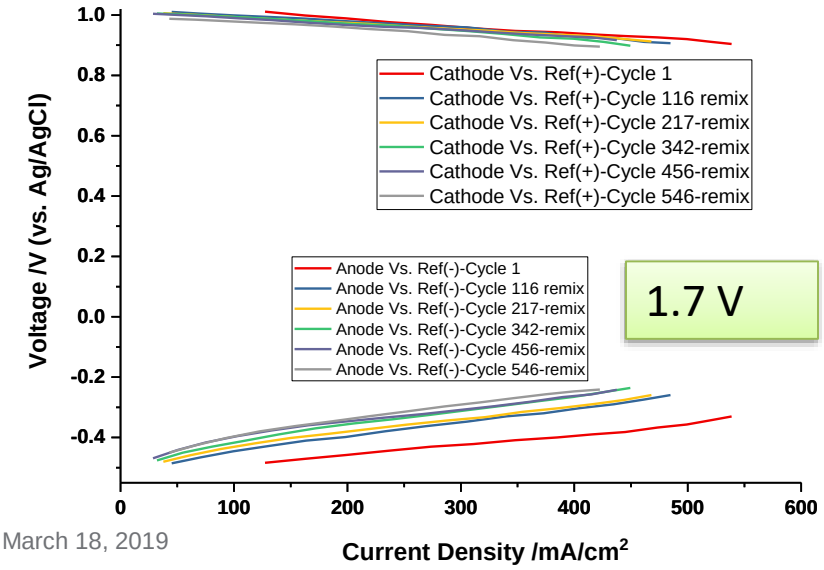




Polarization curves-cathode and anode for remixed solutions

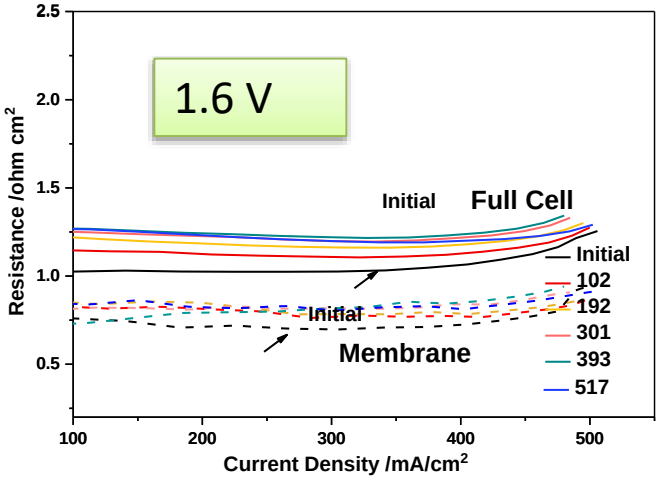




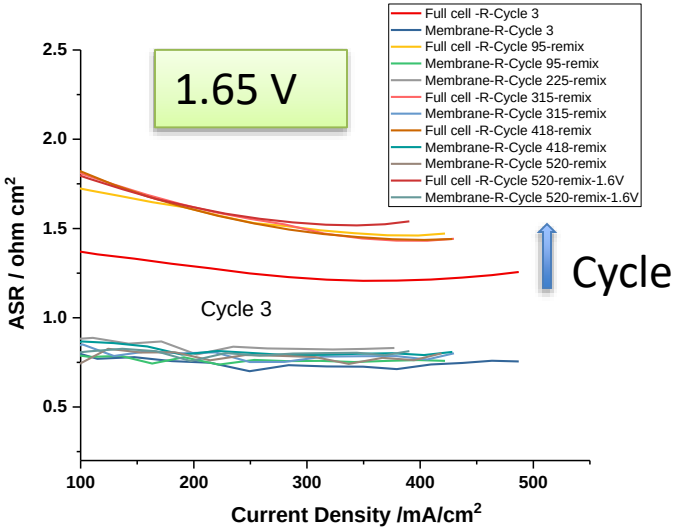


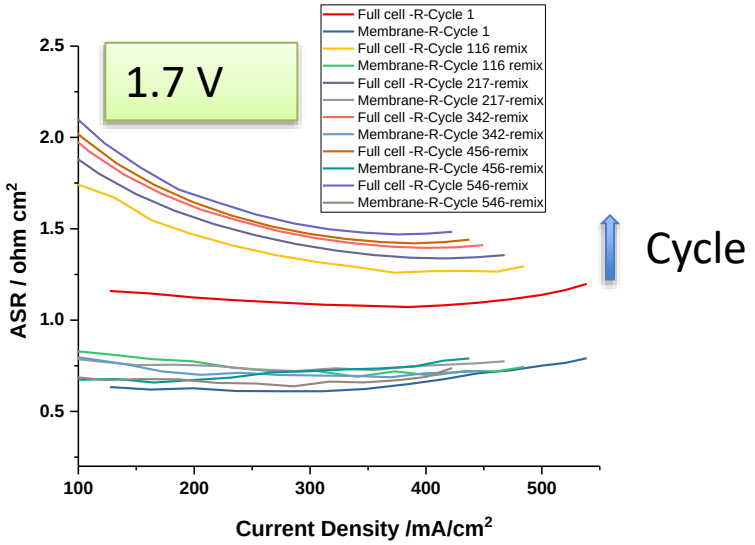
- Performance decay was observed for full cell polarization mainly due to anode.
- Higher upper voltage can result in more significant anode decay.

Resistances for remixed solutions



- The resistances of full cell gradually increased over cycling.
- The resistances of membranes after cycling is larger than that of original one and then keep constant over cycling.
- Higher upper voltage can lead to enhanced full cell resistances.

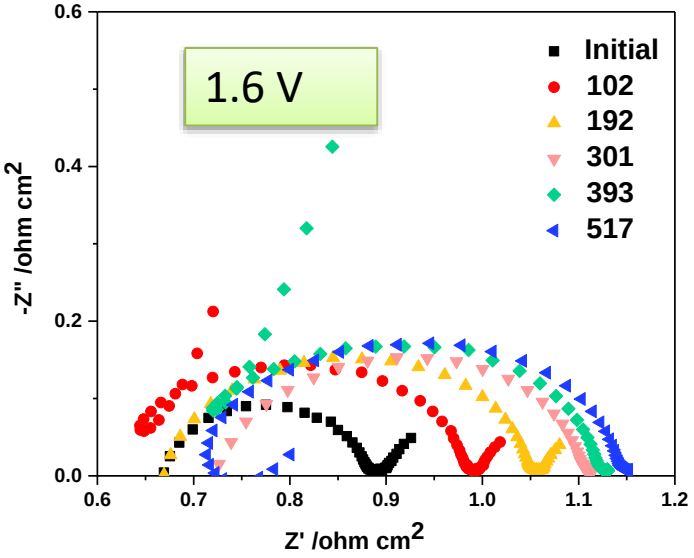


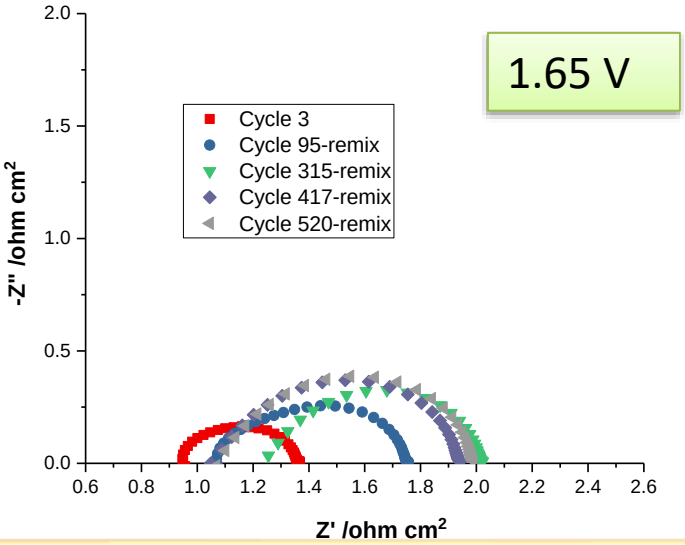


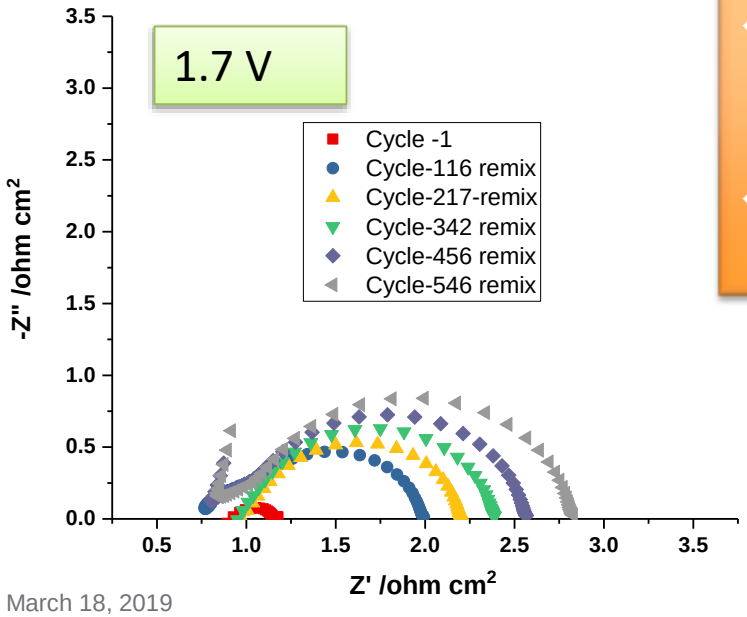
Full Cell R= $(OCV-V_{output})/I$

Membrane R= $(V_{cathode\ vs.\ Ref\ (+)}-V_{cathode\ vs.\ Ref\ (-)})/I$

Ac impedances for remixed solutions



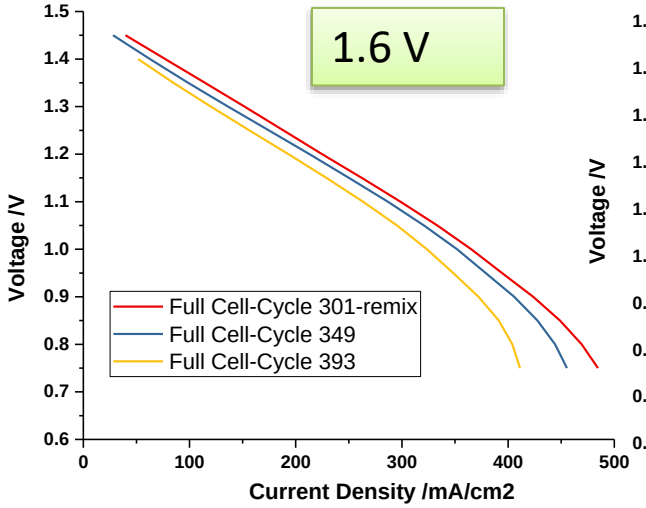


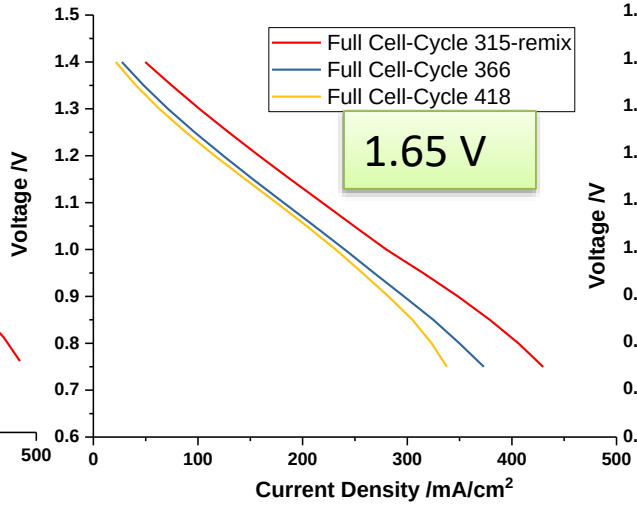


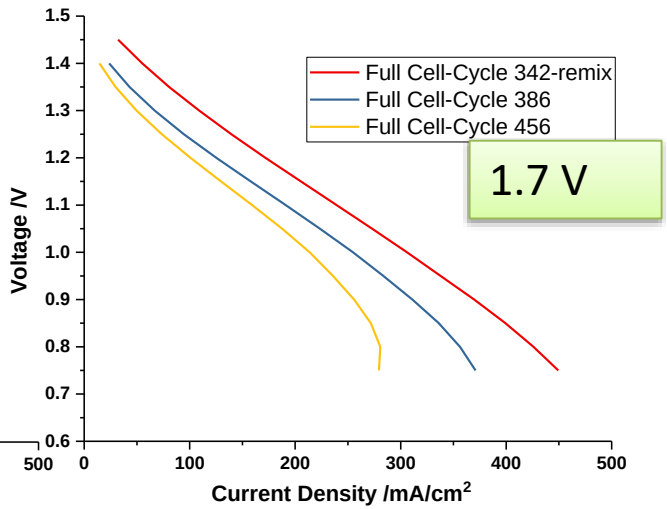
- The enhancement of resistances over cycling mainly results from the increasing charge transfer resistances.
- Higher voltage can lead to greatly improved charge transfer resistances

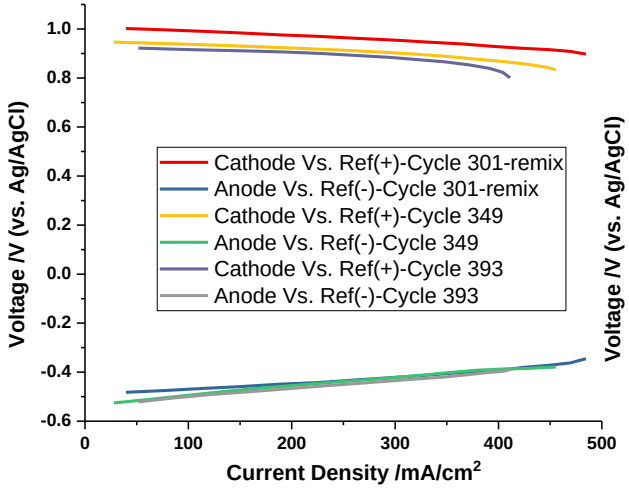
	1.60 V	1.65 V	1.70 V
ΔR-charge transfer resistances/ohm cm^2	0.15	0.6	1.5

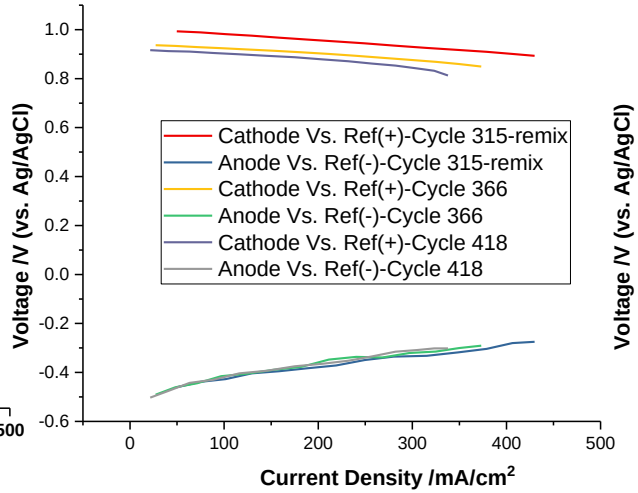
Polarization curves for cycles from 300 -400

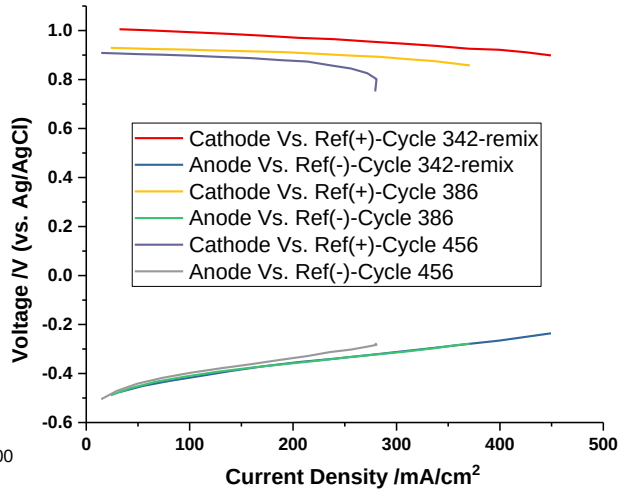






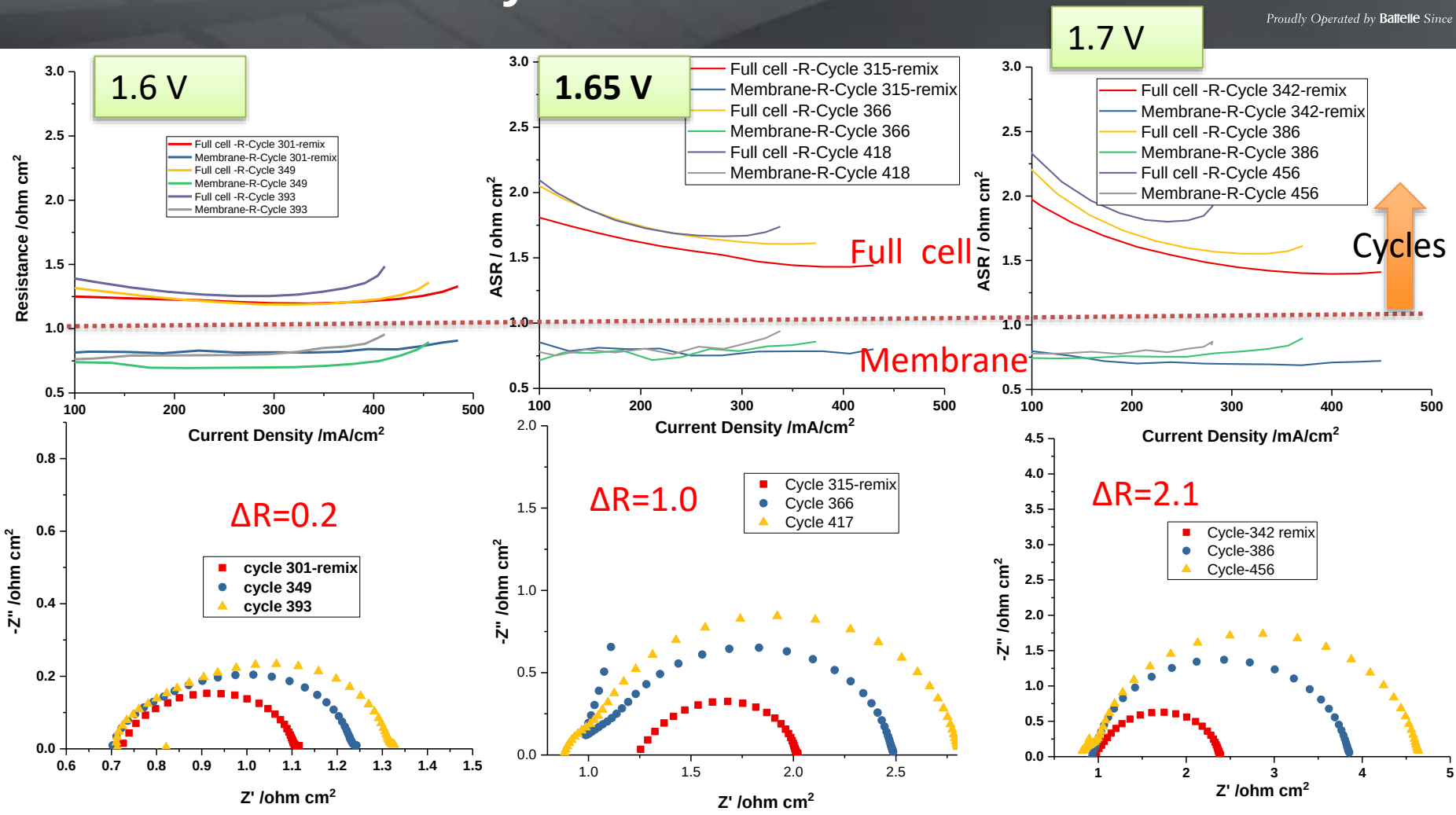






- Voltage decays with increasing cycles due to cathode.
- Higher upper voltage can lead to enhanced cathode voltage degradation.

Resistances for cycles from 300 -400



- The resistances of full cell gradually increased over cycling mainly due to increasing charge transfer resistances.
- The resistances of membranes keep constant over cycling.
- Higher upper voltage can lead to greatly increasing changes of full cell resistances due to increasing changes of charge transfer resistances.

Conclusions

- Higher upper voltage can cause more significant performance decay (e.g. VE and capacity)
- Remixing after every 100 cycles can only affect anode performance. Cathode performance and membrane resistances almost keep constant. Higher upper voltage could lead to more obvious anode decay.
- For every 100 cycles, cathode performance decays with increasing cycles. However, there is no significant influence on anode performances. Higher upper voltage could result in more significant cathode decay.

Future plans

- Correlation between cell performances and electrolyte composition or electrode or bipolar plates properties over cycling.

- Other stressors study

Acknowledgements

- Financial support from the US Department of Energy's Office of Electricity.

- Beneficial discussions with **Dr. Imre Gyuk** of the DOE-OE Grid Storage Program and team members (Chaojie Song, Zhengming Jiang, Alison Platt, Liz, Khalid Fatih, Christina Bock, Darren Jang) from **National Research Council Canada**.