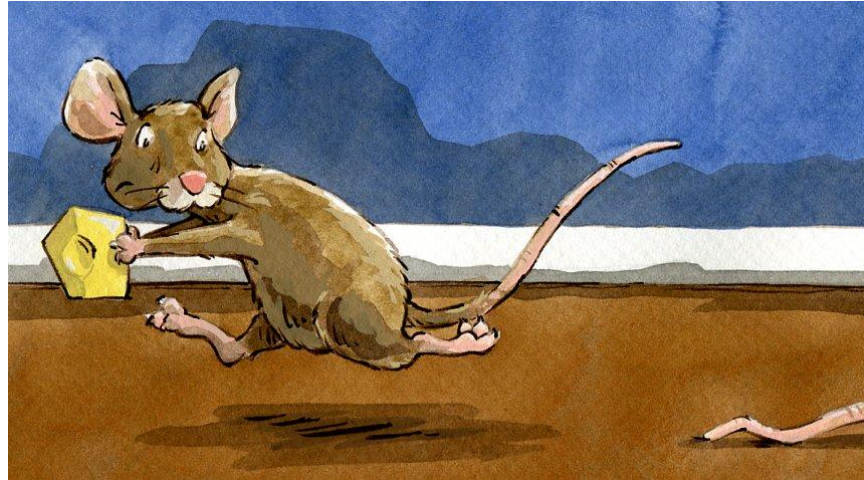# Accelerated Aging Methods for Evaluating Carbon Electrode Materials

IEEE Conference on Technologies for Sustainability
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Pavel Mardilovich
Alex Yokochi

Outline

Introduction

1. Motivation for this work

2. Batteries and cycle life comparison

3. Commercially available Redox Flow Batteries (RFBs)

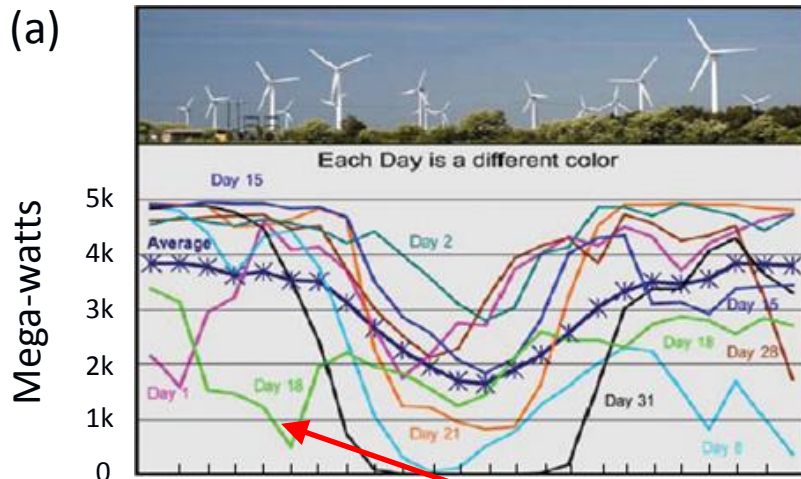4. Importance of accelerated aging in these types of batteries

Experimental

1. Setup and reaction vessel assemblies

2. Assessing degradation via continuous charge mode experiments
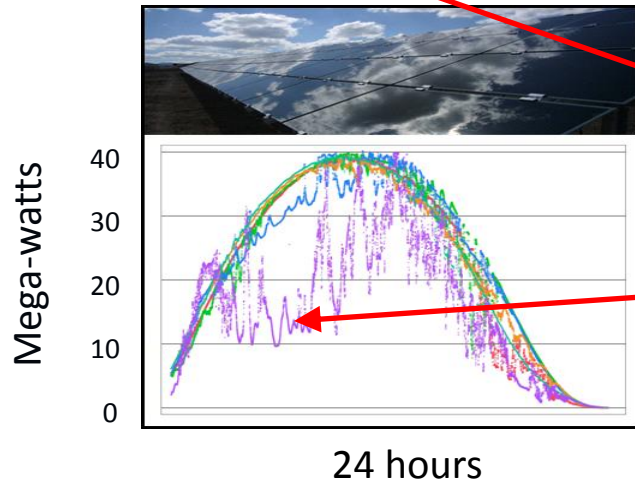
3. Preliminary results and discussion

Conclusions/Future Work

Intro: intermittent power

(a)

Each Day is a different color

Mega-watts: 5k, 4k, 3k, 2k, 1k, 0

Day 15, Average, Day 2, Day 18, Day 26, Day 1, Day 18, Day 21, Day 31, Day 8

(b)

Mega-watts: 40, 30, 20, 10, 0

24 hours

(a) Daily profiles of wind power projected by 7x output in April 2005 for the year 2011 in Tehachapi, Califonia (**Courtesy of ISO California**). The canyon mid-day is characteristic of wind power generation.

(b) PV power over a span of 6 days in Spain (**Courtesy of AES**). The sudden drops are due to cloud cover. NOTE how wind and solar complement each other.
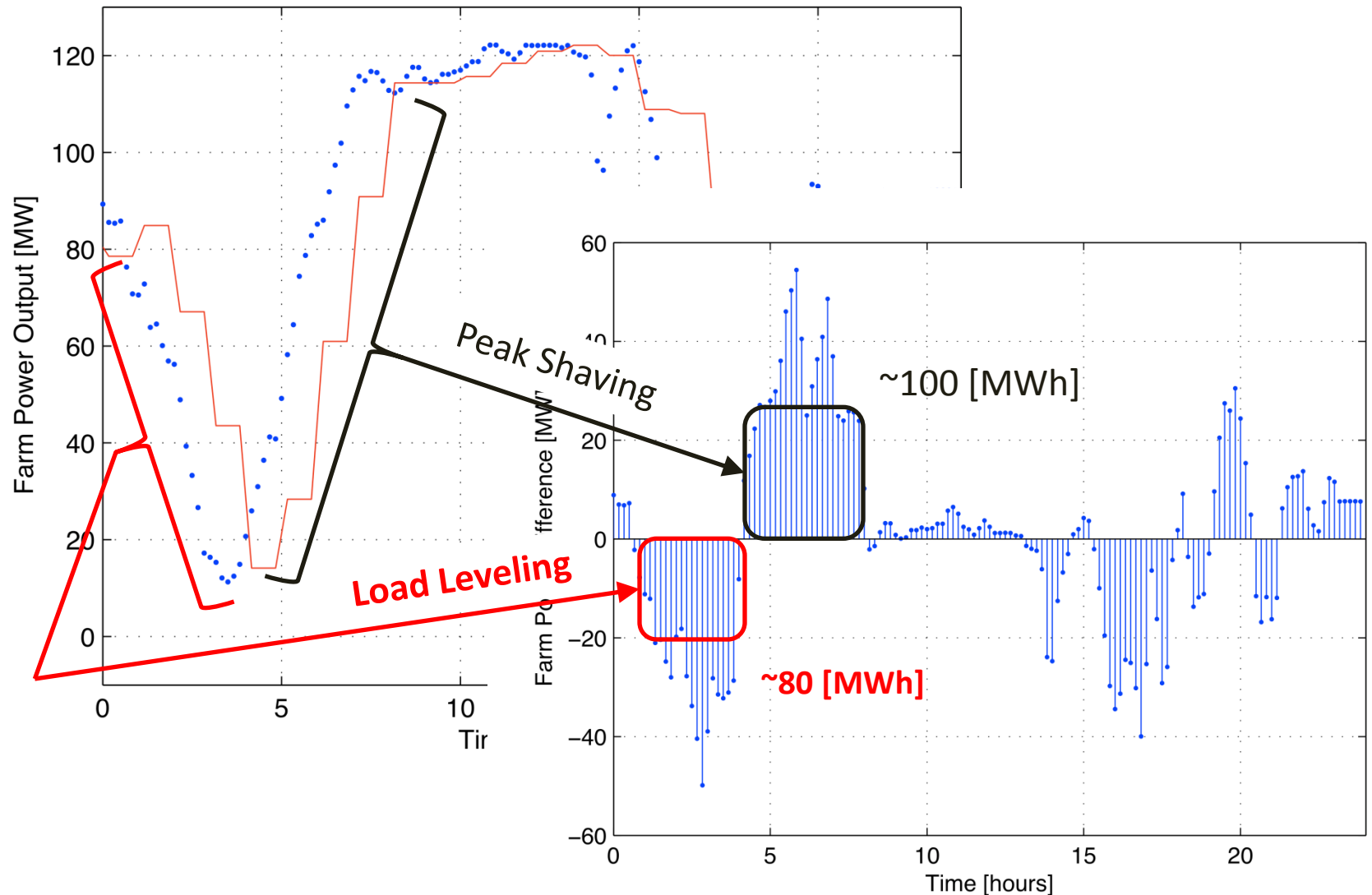
Sometimes the wind doesn't blow

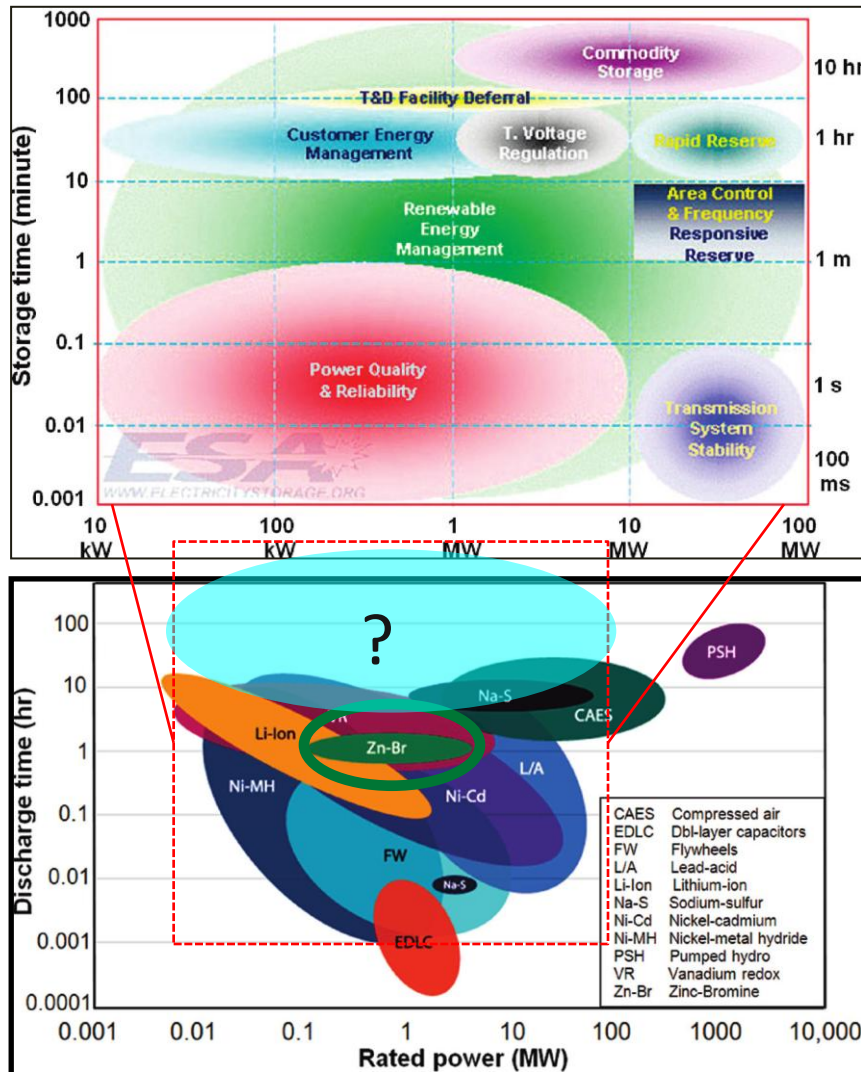**Cloud cover is devastating to solar**

Intro: wind penetration
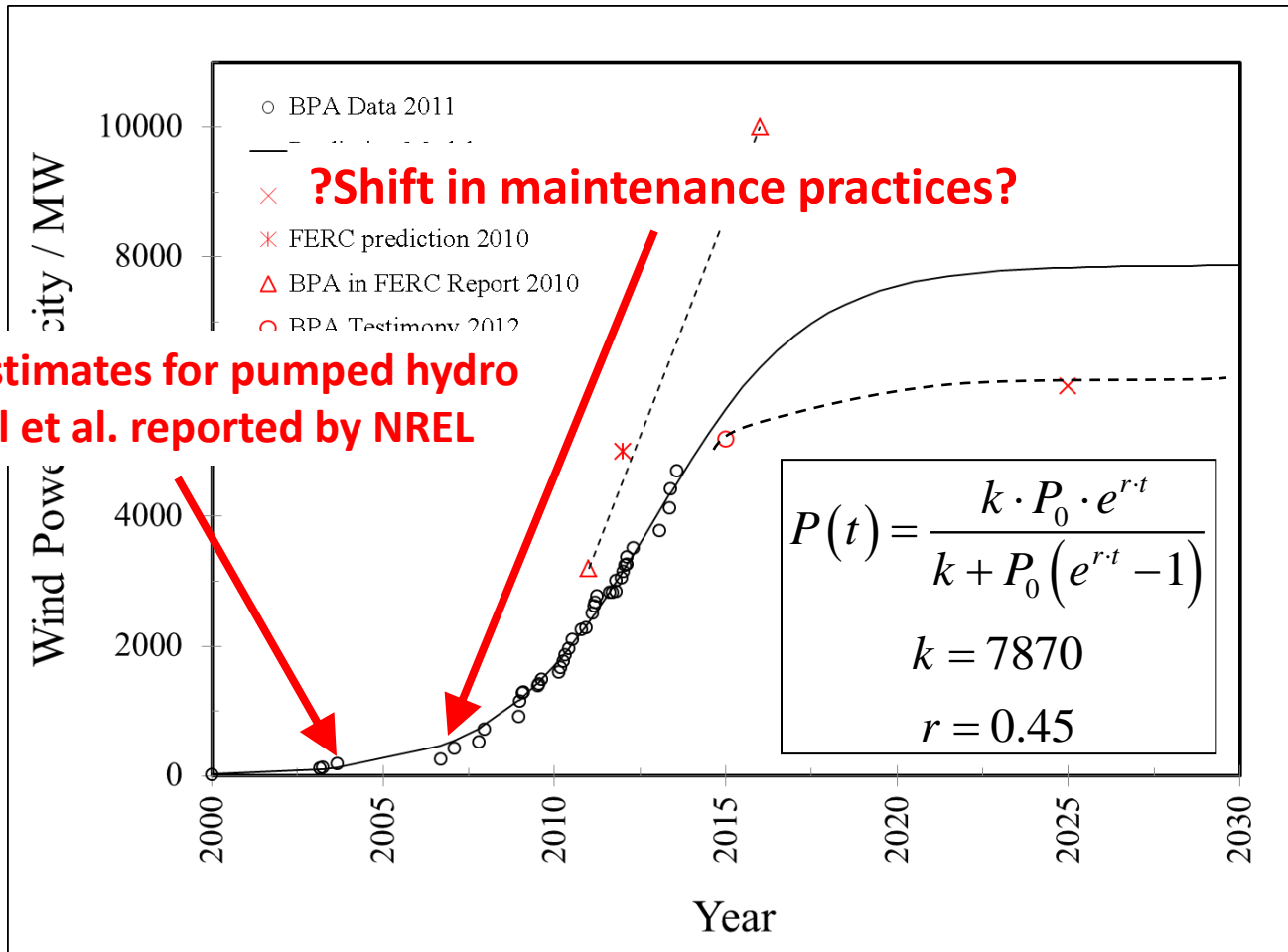
Introduction: need for big batteries

Intro: power management

As depicted in the top figure, there is a wide range of power management <u>needs</u>. The broadest of which is clearly **Renewable Energy Management**.

The figure below shows the expected ranges for some <u>available</u> technologies.

NOTE the combined spectrum does not cover the entire power needs spectrum.

…Hybrid Energy Storage Systems (HESS)…

Figures Courtesy of ESA
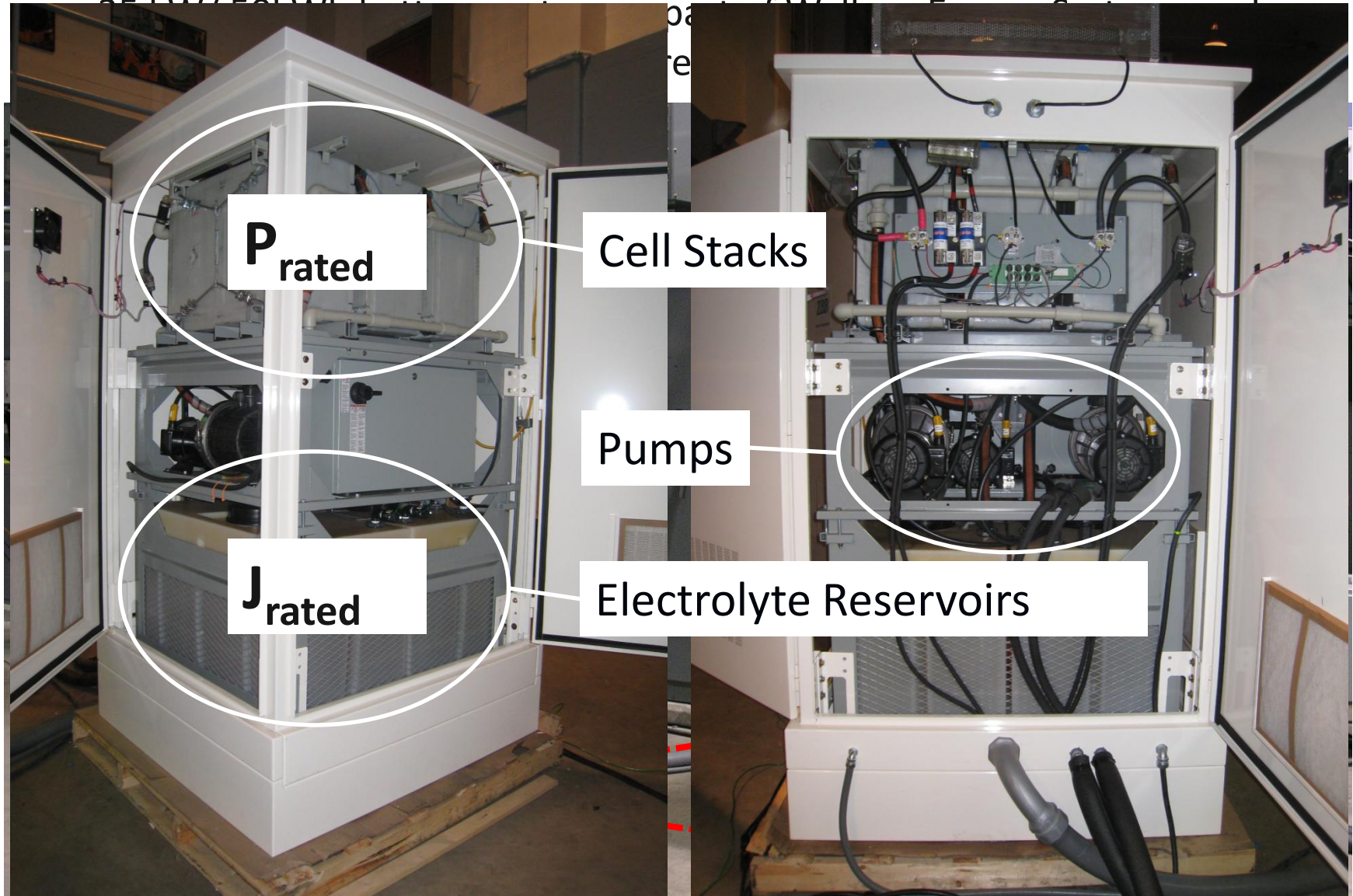http://www.electricitystorage.org/ESA/home/

Intro: battery technologies

Type	OCP	Specific Energy	Operating Temperature	Discharge Time	Self-discharge % per month	Cycle-life	Round-trip Efficiency
	V	Wh/kg	° C	hrs	@ 20 ° C	Deep	%
LAB	2.1	25-40	-40 – 60	up to 8	4 – 50	1K	50 – 75
NCB	1.35	30-45	-10 – 45	up to 4	5 – 20	2K	55 – 70
VRB	1.4	10-20	10 – 40	4 – 12[b]	3 – 9	5K	65 – 80
LCB	2.1	25-40	-40 – 60	up to 4	-	3K	-
Na-S	2.1	150-240	300 – 350	4 – 8	Negligible	4K	75 – 90
ZEBRA	2.6	95-120	300 – 350	4 – 8	Negligible	3K	75 – 90
C-LC	3.4	155	-25 – 40	up to 4	2	1K	94 – 99
LT-LFP	1.7	50-70	-25 – 40	up to 4	2	4K	94 – 99
ZBB	1.85	75	-30 – 50	4 – 12[b]	<10[c]	5K	75 – 85

[a] LAB: lead-acid batteries; NCB: nickel-cadmium batteries; VRB: all-vanadium redox flow batteries; LCB: lead-carbon ultrabatteries; Na-S: sodium-sulfur batteries; ZEBRA: Zeolite Battery Research Africa; C-LC: lithium-ion batteries of carbon anode and $LiCoO_2$ cathode; LT-LFP: lithium-ion batteries of $Li_4Ti_5O_{12}$ anode and $LiFePO_4$ cathode; ZBB: zinc bromide flow batteries
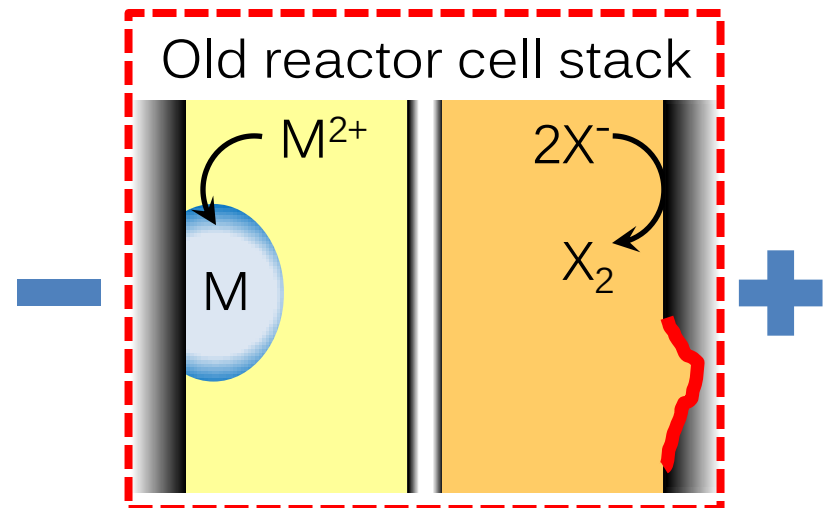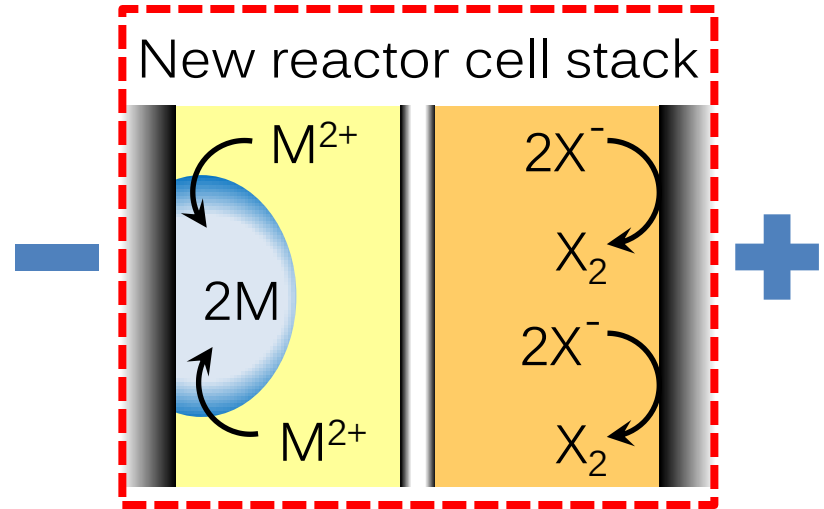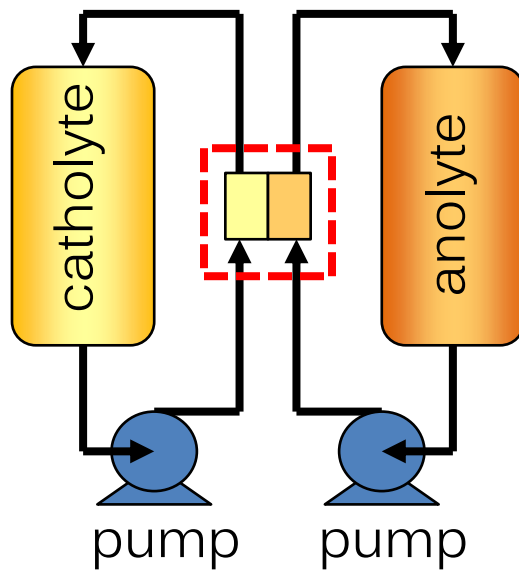
[b] This is dependent on the electrolyte reservoirs and can be engineered to be more than the listed values

[c] The reactors must be drained when not in use

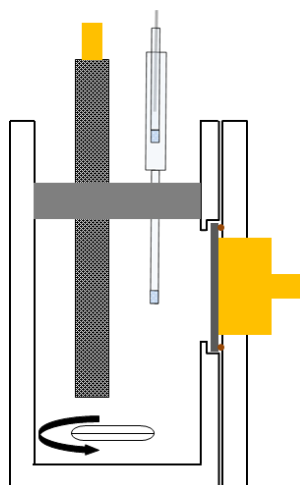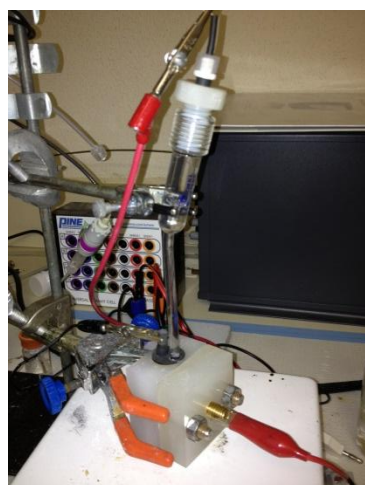Handbook of Energy Storage for Transmission and Distribution Applications, ESA, Barton and Infield IEEE Trans. Energy Convers 2004, http://www.mpoweruk.com/performance.htm

Intro: Commercial RFB system

P_{rated} — Cell Stacks

J_{rated} — Electrolyte Reservoirs
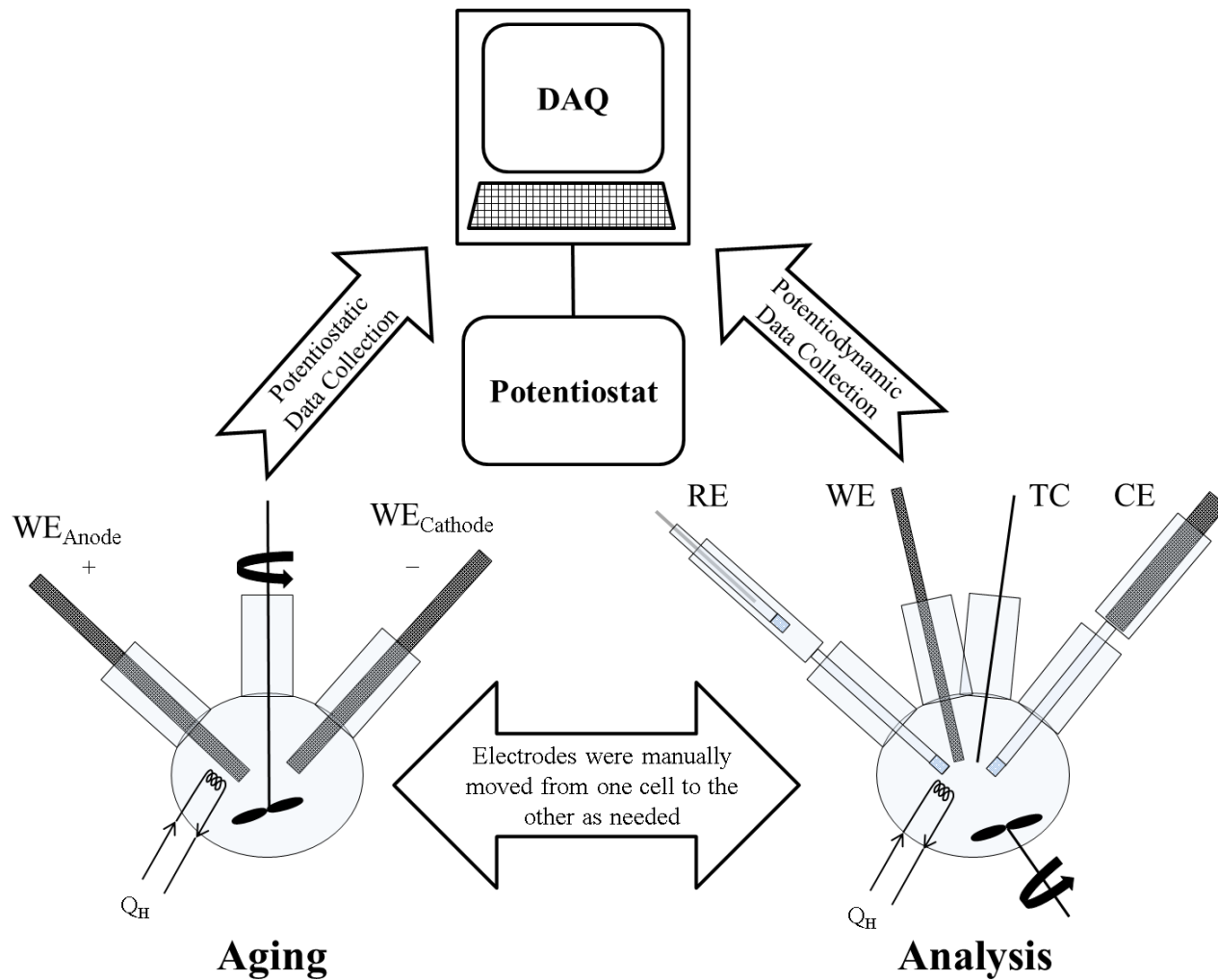
Pumps

Intro: electrode degradation

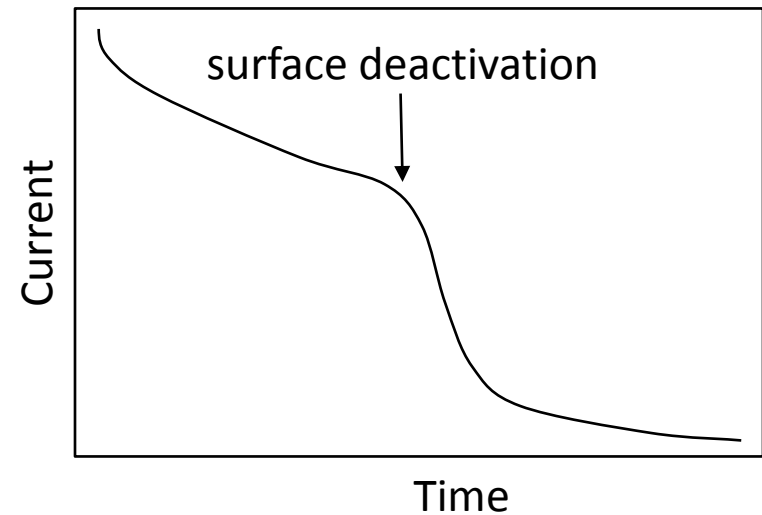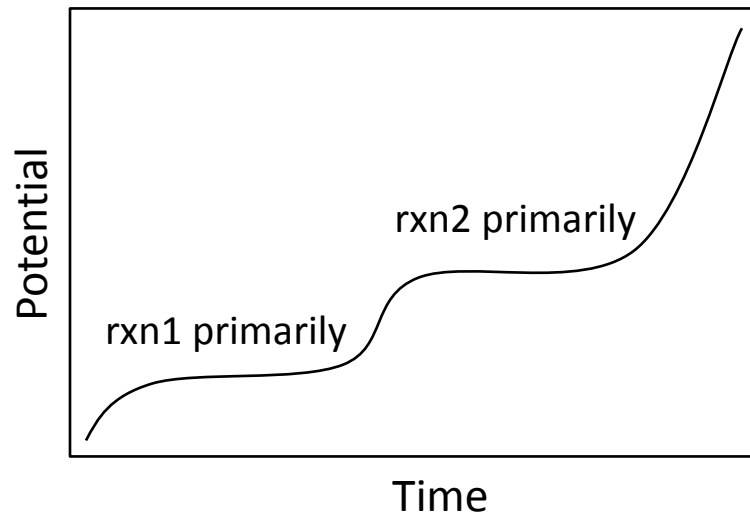# Experimental: reactor assemblies
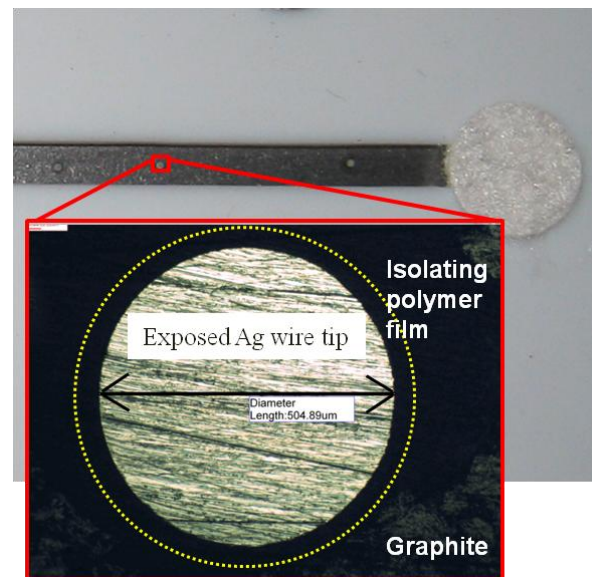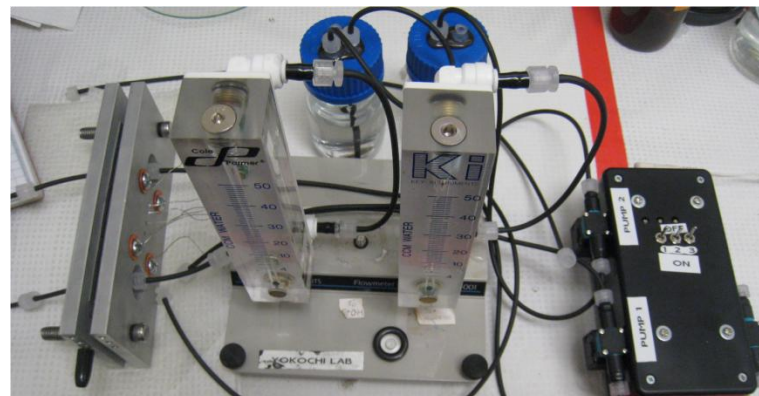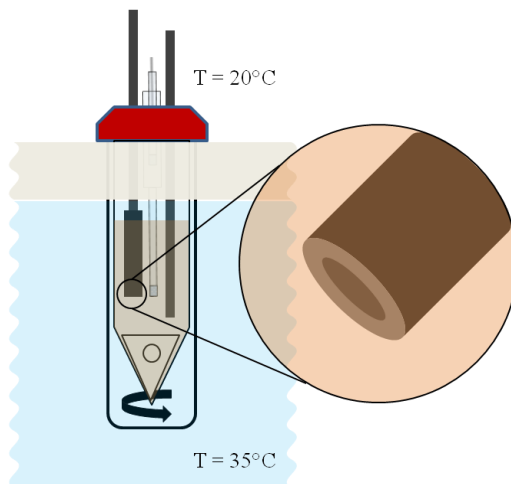
Experimental: general process

Experimental: straightforward method

- Constant current death

- Potential is measured

- Identifiable reactions

- Constant voltage death

- Current is measured

- Observed activity loss

Experimental: a basis for degradation

The Tafel equation is used to fit potentiodynamic data. Since the Tafel equation can be used to model a single reaction under kinetic control, we can use it to model each redox reaction separately in our system (**assume well controlled**).

$$I = I_0 \exp\left(\frac{-\alpha F \eta}{RT}\right)$$

Exchange current, I_0, is proportional to the active sites of a surface available to effect the electrochemical reaction.

$$I_0 \propto k_0$$

The transfer coefficient, α, is closely related to the activation energy of a reaction and evaluates how easily the reaction occurs at these sites, and consequently how much extra energy in the form of voltage is needed to effect the reaction (over-potential).

$$\alpha F \eta \propto E_a$$

Ideally, these parameters will remain constant, though electrode conditioning or 'reaction kinetics' degradation will appear as a change in I_0 and α.

Experimental: potantiostatic
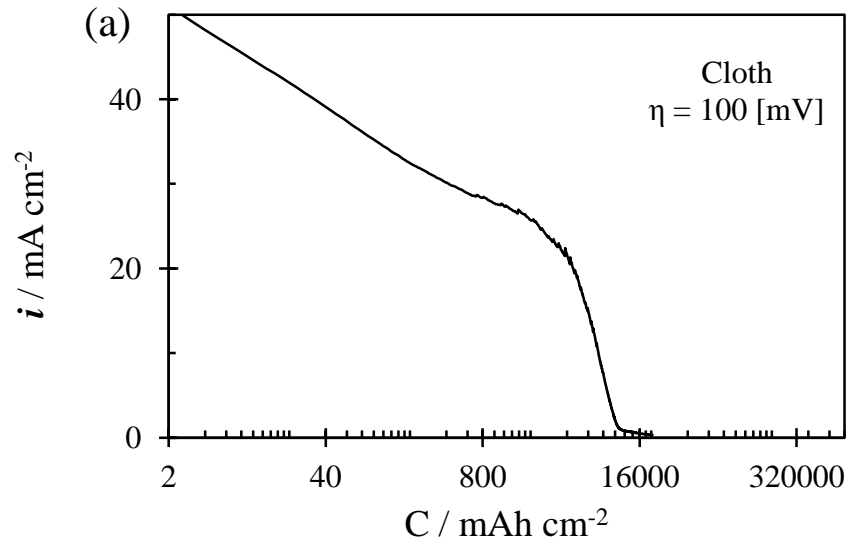
a) Plot showing electrode (cloth) death by applying a constant potential with the straight forward method
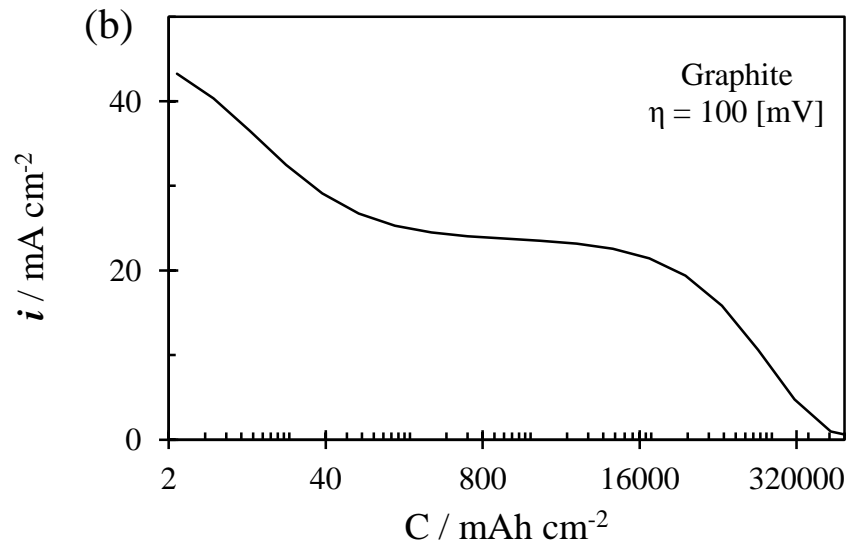
b) Plot showing electrode (sintered graphite) death by calculating the theoretical current from measured Tafel parameters
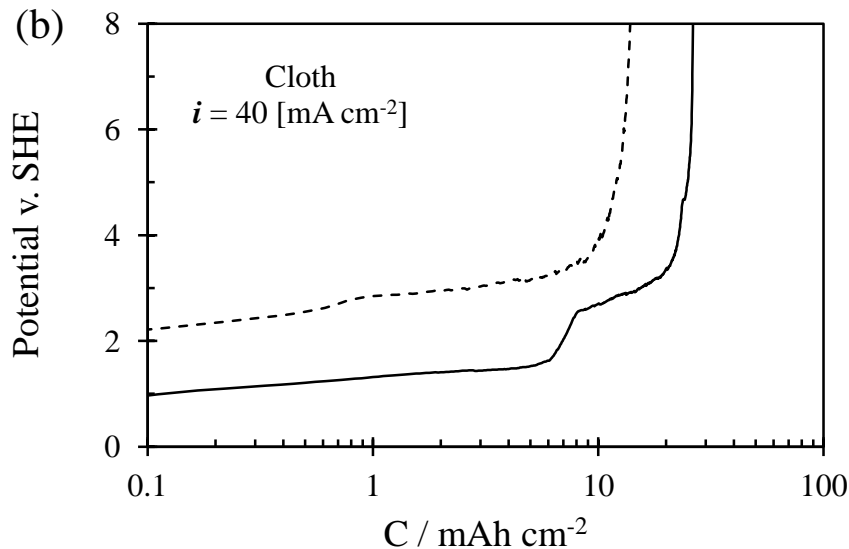
Experimental: galvanostatic

(a)
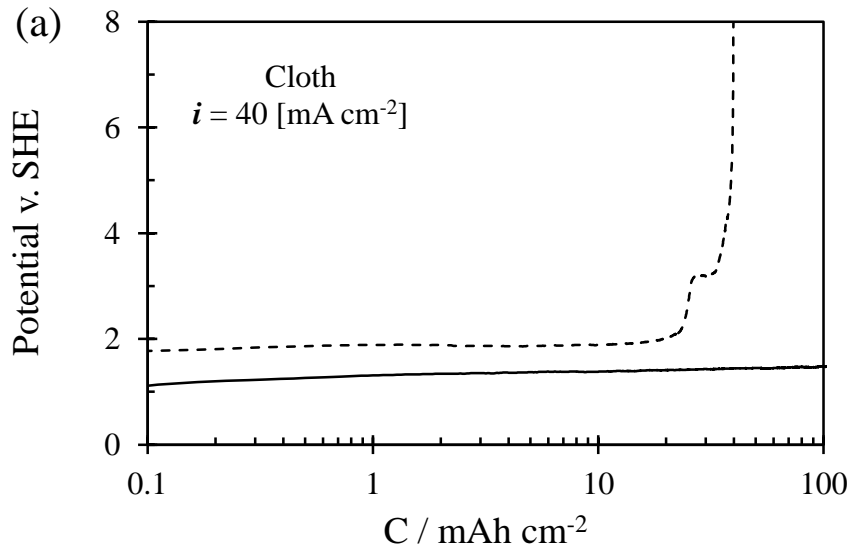
a) Plot showing electrode (cloth) death by applying a constant current for bromide/bromine couple

(b)

b) Plot showing electrode (cloth) death by applying a constant current for chloride/chlorine couple

Experimental: discussion

Observations

- There are two stages of degradation that can be observed by measuring current at a constant potential for sintered graphite and graphitized cloth
  - One involves the irreversible <u>oxidative damage</u> arising from continuous oxidation of the anion species
  - And the second is likely due to the undesired <u>electrolysis of water</u>
- The individual stages for the straightforward method differ in onset as might be expected because the oxidation of chloride occurs outside the water oxidation window
  - This in turn suggests that using KCl as an aging bath for accelerated aging of electrodes in an aqueous electrochemical system may be misleading and unrepresentative

Suggested alternative

- Collect potentiodynamic data throughout the aging test to provide insight as to the degradation mechanism(s) predominantly responsible for degradation at each stage
- Pre-oxidize the electrode surface with an electrochemically inactive anion species that has a tendency to also intercalate – this can be expected to catalyze the undesired water electrolysis reaction even in representative electrolyte baths
- Remove the more vulnerable active sites by a peroxide rinse prior to aging

Conclusion and future work

Conclusions

- The potentiodynamic data collection method allowed for greater insight of individual degradation mechanisms
  - By measuring the model parameters directly, consideration whether the degradation is due to the elimination of active surface sites or undesired surface chemistry, is made possible
- Pre-oxidation of carbon surface catalyzes the undesired water electrolysis reaction
  - Pre-oxidizing the electrode surface with a strong oxidizing agent can further shorten the aging duration
- A quantitative assessment of charge passed through an electrode surface for a certain (isolated) undesired reaction can be used to generate a cycle life model that can accurately predict the number of cycles it would take to reach a standard level of poor battery performance
  - From the preliminary evaluation it was determined that the parameters involved in this calculation would include at minimum the following: 1) the operating current density, 2) the percent capacity being cycled on average, and reaction ratio between the desired and undesired reaction.

Future Work

- Establish the effect current density has on the electrochemical reaction ratio for a given electrochemical system and measure the charge required to observe surface deactivation
  - By performing a series of potentiostatic deaths at various applied over-potentials
- Test various chemical pre-treatments that may favorably shift the reaction ratio
  - Pre-oxidizing the electrode surface with a strong oxidizing agent and activating the surface

Acknowledgements

Thanks!

Questions?

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