Investigation of Electrically Conductive Aqueous Solutions

for De-energizing Lithium-Ion Batteries

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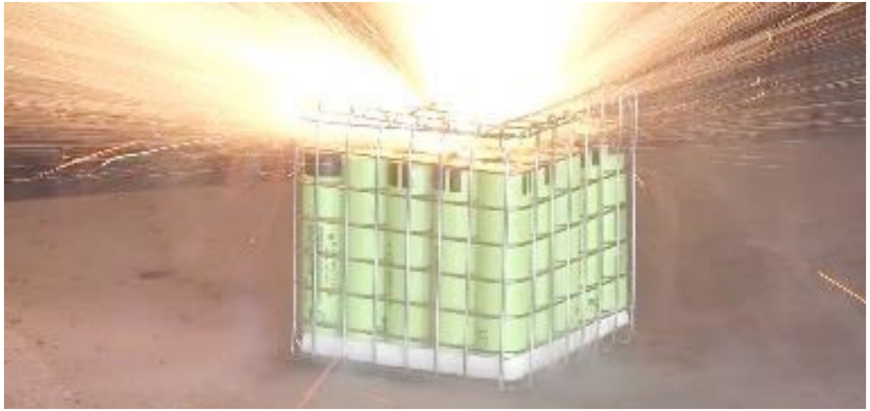
Why is discharging lithium-ion cells prior to disposal important?

- Necessary for stabilization
- Prevent explosions, fires and toxic gas emission
  - Damage disposal infrastructure
  - Reduce the recycling value and materials reclamation



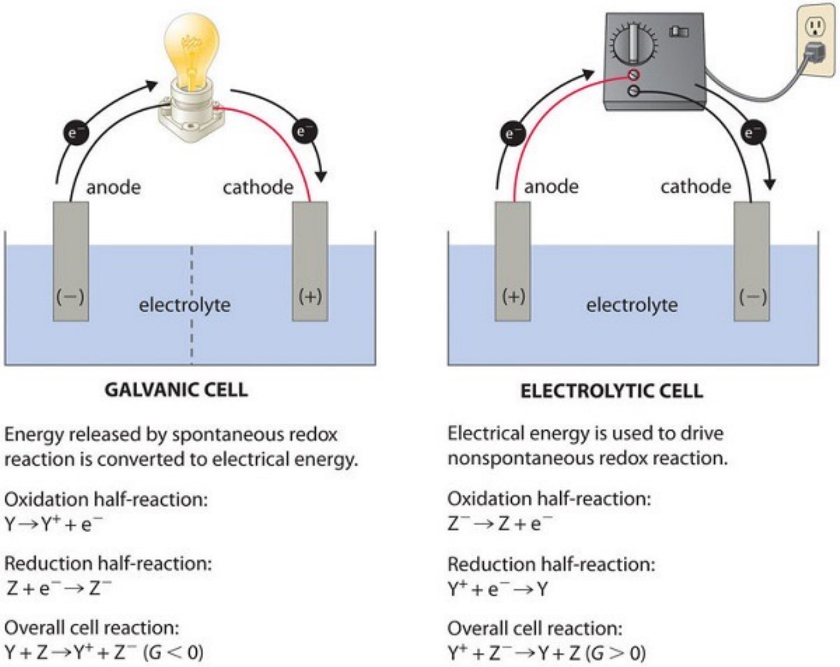
Previous method – sodium chloride (salt) solution

- Dissolution of battery cell materials
- Solution disposal issue after use → contamination
    - Lithium ion and lithium metal battery modules and cells are listed as Class 9 Miscellaneous hazardous materials in the U.S.
    - International hazardous materials (dangerous goods) regulation
- Electrode terminals dissolved prior to complete discharge
    - Prevents measurement of residual cell charge

Tasks for research work

- Identify alternative conductive solutions for immersion discharge of lithium-ion cells
- Evaluate the performance of these solutions in terms of deterring the dissolution of cell materials
- Support that an alternative solution will work in practice on lithium-ion cells and provide better performance than sodium chloride
  - Less dissolution of cell material and without breaching the cell case

Reaction Responsible (Electrolysis)



GALVANIC CELL

Energy released by spontaneous redox reaction is converted to electrical energy.

Oxidation half-reaction:
$Y \rightarrow Y^+ + e^-$

Reduction half-reaction:
$Z + e^- \rightarrow Z^-$

Overall cell reaction:
$Y + Z \rightarrow Y^+ + Z^-$ $(G < 0)$

ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

Oxidation half-reaction:
$Z^- \rightarrow Z + e^-$

Reduction half-reaction:
$Y^+ + e^- \rightarrow Y$

Overall cell reaction:
$Y^+ + Z^- \rightarrow Y + Z$ $(G > 0)$

- oxidation half-reaction occurs at anode, and the reduction half-reaction occurs at cathode
- Depending on the oxidation reactions at the anode (and if battery voltage sufficient), the anode may react with the electrolyte and lose mass

Libretexts. “20.3: Voltaic Cells.” Chemistry LibreTexts, Department of Education Open Textbook Pilot Project, 18 Sept. 2019, chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/20%3A_Electrochemistry/20.3%3A_Voltaic_Cells.

Eight potential conductive solutions

Designation	Electrolyte	Concentration (g/L)	pH
A	Sodium chloride	30.5	7.48
B	Sodium chloride + sodium hydroxide	19.1 NaCl + 3.6 NaOH	13.01
C	Calcium chloride	41.4	10.31
D	Sodium bicarbonate	77.9	8.55
E	Ammonium bicarbonate	52.3	8.38
F	Monosodium phosphate	207.0	4.19
G	Monopotassium phosphate	107.8	4.34
H	Ammonium dihydrogen phosphate	98.5	4.39

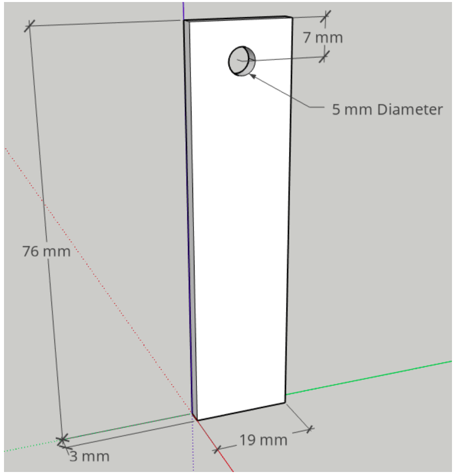
- Three chloride solutions
  - Addition of lye for increased alkalinity
- Two bicarbonates
- Three mildly acidic monobasic hydrogen phosphates
- Formulated for same conductivity, 50 mS/cm
- Solutions of deionized water

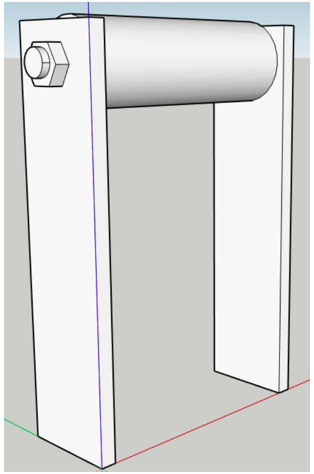
Shaw-Stewart, James, et al. “Aqueous Solution Discharge of Cylindrical Lithium-Ion Cells.” Sustainable Materials and Technologies, Elsevier, 25 Apr. 2019.

Y. Feng, K.S. Siow, W.K. Teo, K.L. Tan, A.-K. Hsieh, Corrosion Mechanisms and Products of Copper in Aqueous Solutions at Various pH Values, CORROSION. 1997;53(5):389-398.

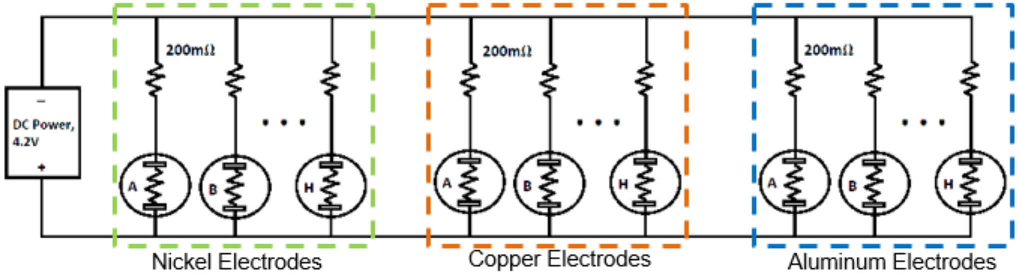
Metal electrodes representative of cell materials

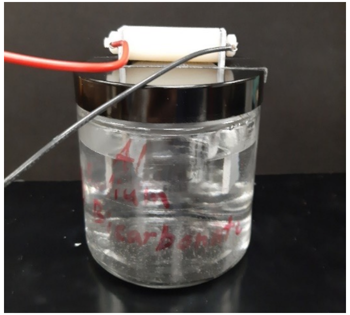
- Pairs of electrically connected electrodes to simulate cell materials positively and negatively charged across a cell
- Goal is to measure mass loss of materials common to lithium-ion cell exterior (case and electrodes) → prevent breach
  - Nickel, copper and aluminum





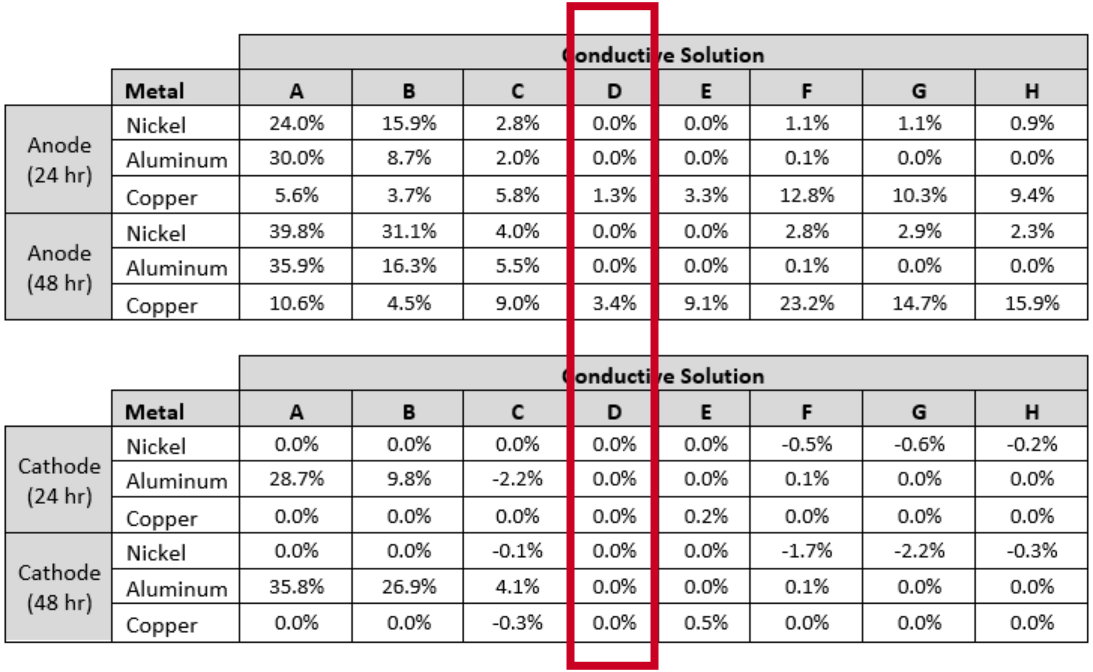
Experimental setup





- Pairs of electrodes from each material are submerged in jars containing each conductive solution
- 4.2 V applied across each pair of electrodes
  - Simulates the presence of the charge from a common lithium-ion cell
- 24 hour and 48-hour exposure times
- Mass of electrodes measured before and after exposures to measure mass loss

Comparing mass loss in conductive solutions



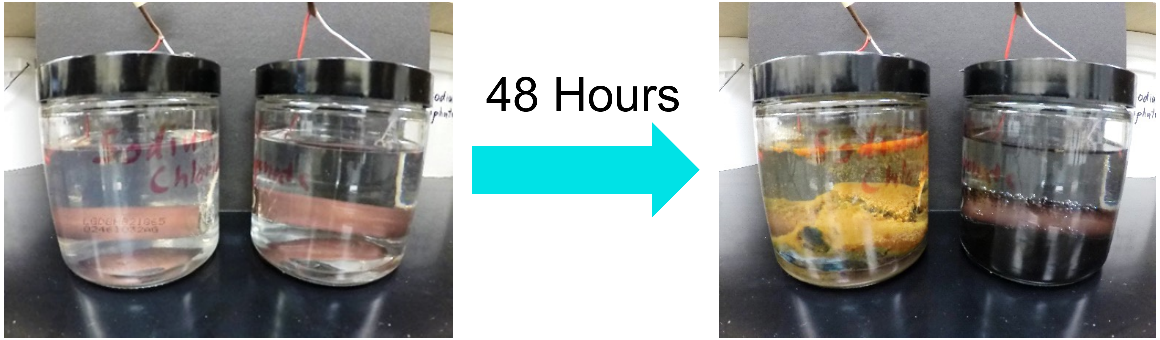
		Conductive Solution							
	Metal	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**
Anode (24 hr)	Nickel	24.0%	15.9%	2.8%	0.0%	0.0%	1.1%	1.1%	0.9%
	Aluminum	30.0%	8.7%	2.0%	0.0%	0.0%	0.1%	0.0%	0.0%
	Copper	5.6%	3.7%	5.8%	1.3%	3.3%	12.8%	10.3%	9.4%
Anode (48 hr)	Nickel	39.8%	31.1%	4.0%	0.0%	0.0%	2.8%	2.9%	2.3%
	Aluminum	35.9%	16.3%	5.5%	0.0%	0.0%	0.1%	0.0%	0.0%
	Copper	10.6%	4.5%	9.0%	3.4%	9.1%	23.2%	14.7%	15.9%

		Conductive Solution							
	Metal	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**
Cathode (24 hr)	Nickel	0.0%	0.0%	0.0%	0.0%	0.0%	-0.5%	-0.6%	-0.2%
	Aluminum	28.7%	9.8%	-2.2%	0.0%	0.0%	0.1%	0.0%	0.0%
	Copper	0.0%	0.0%	0.0%	0.0%	0.2%	0.0%	0.0%	0.0%
Cathode (48 hr)	Nickel	0.0%	0.0%	-0.1%	0.0%	0.0%	-1.7%	-2.2%	-0.3%
	Aluminum	35.8%	26.9%	4.1%	0.0%	0.0%	0.1%	0.0%	0.0%
	Copper	0.0%	0.0%	-0.3%	0.0%	0.5%	0.0%	0.0%	0.0%

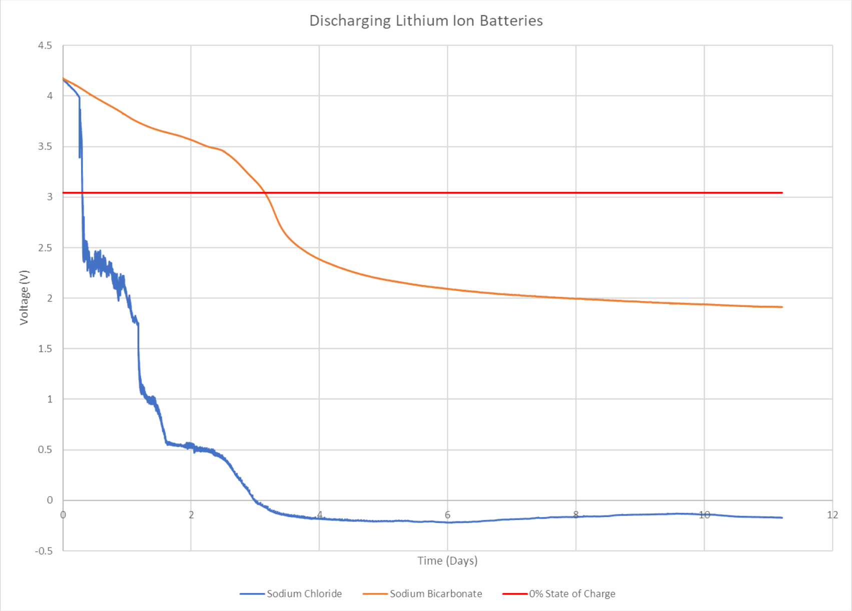
- Sodium chloride solution – highest mass loss for nickel and aluminum
- The lowest mass loss for all three materials – **sodium bicarbonate** solution (aka baking soda)

18650 Lithium-ion cells in sodium chloride and sodium bicarbonate solutions

- Fully charged 18650 lithium-ion cells immersed in solutions of sodium chloride and sodium bicarbonate with deionized water, 50 mS/cm
- Observed substantial dissolution of the cell in the sodium chloride solution but not in the sodium bicarbonate solution
  - Evidence of dissolution includes discoloration of water and buildup of sediment



Lithium-ion cells in sodium chloride and sodium bicarbonate solutions



- Rapid decrease in voltage in sodium chloride may be linked to dissolution of the electrodes rather than internal voltage
- 0% SoC in sodium bicarbonate after ~3 days

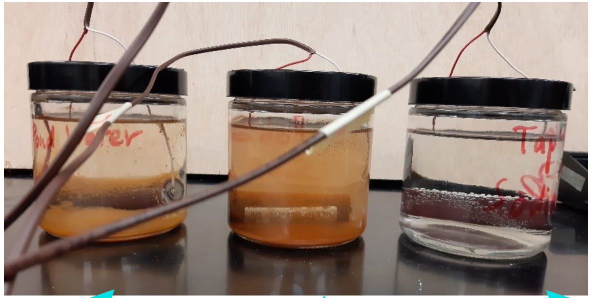
Lithium-ion cells in sodium bicarbonate tap water vs. “dirty” water

- Previous tests indicate that a sodium bicarbonate solution is a viable candidate for immersion discharging of cells
- Assess whether “dirty” water or tap water are viable options to use while continuing to deter cell dissolution
- Cells were then discharged in “dirty” water, “dirty” water with sodium bicarbonate, and Municipal water with sodium bicarbonate
- Sodium bicarbonate solutions at max solubility at 23 degrees C, 53.5 mS/cm

Water source	Water conductivity (mS/cm)	Water pH	$NaHCO_3$ added (g/L)	Solution conductivity (mS/cm)	Solution pH
“Dirty” Water	1.047	8.03	0	1.047	8.03
“Dirty” Water	1.047	8.03	125	53.4	8.92
Tap Water	0.332	7.77	125	53.6	8.44

Lithium-ion cells in sodium bicarbonate tap water vs. “dirty” water

- Six-day immersion – stopped because voltages stabilized
- After immersion, cells in “dirty” water and “dirty” water with sodium bicarbonate showed visible signs of dissolution
- Cell in municipal “tap” water did not show visible signs of dissolution



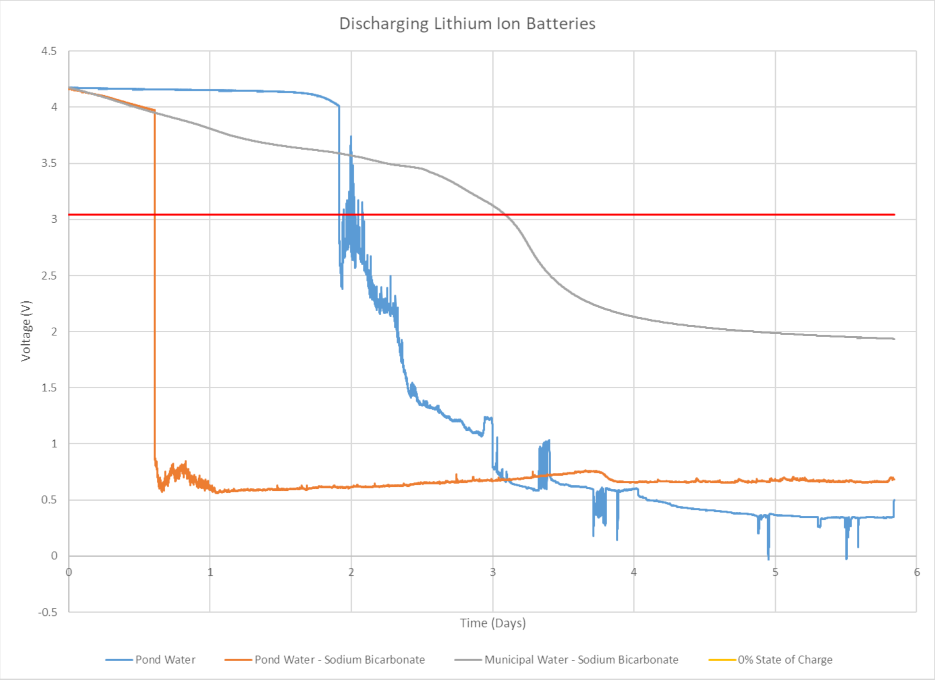
6 days immersion

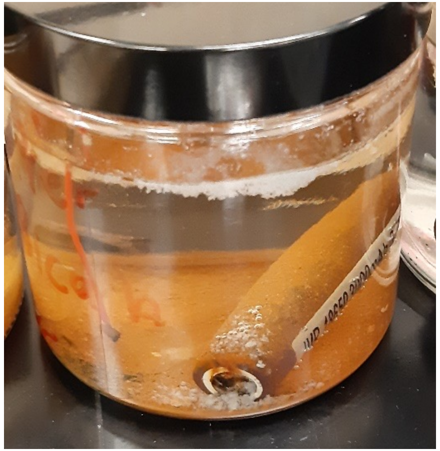
“Dirty” water

“Dirty” water
+ Sod. bicarb.

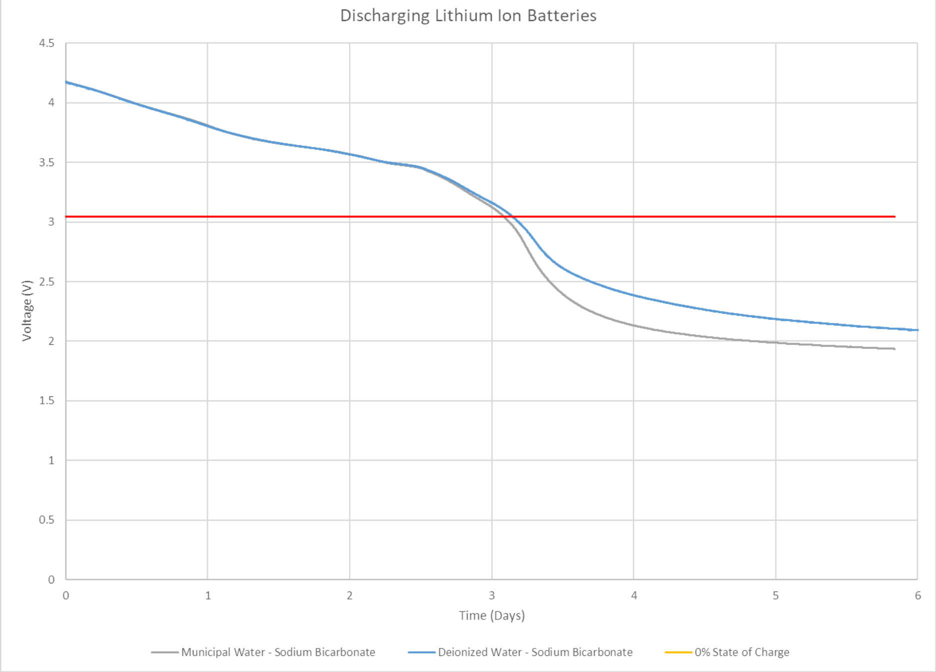
Tap water
+ Sod. bicarb.

Lithium-ion cells in sodium bicarbonate tap water vs. “dirty” water





Lithium-ion cells – Tap water (53.5 ms/cm) vs. deionized water (50.0 ms/cm)



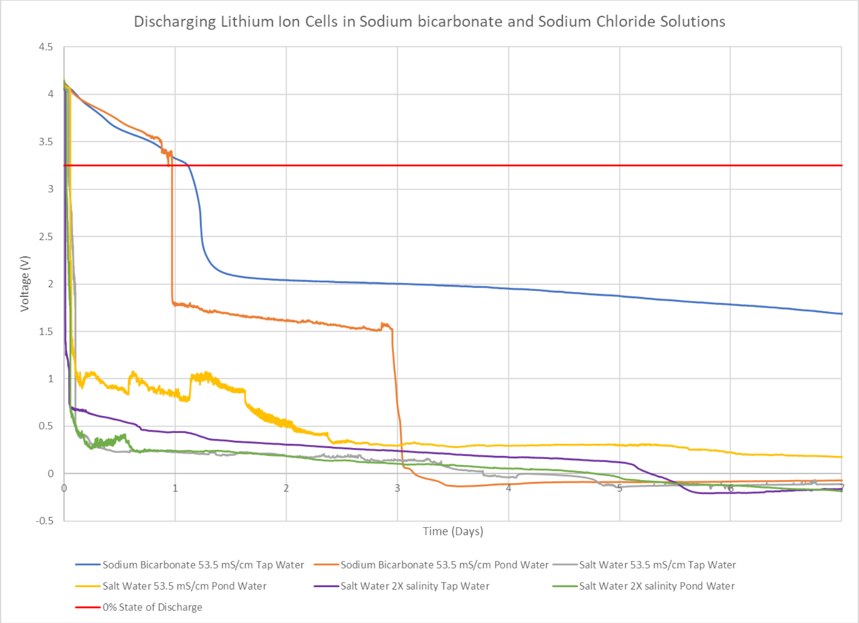
- Not much difference in amount of time it takes to get to 0% SoC
- Additional sodium bicarbonate to get above 50 mS/cm does not contribute to a substantial increase in discharge rate

Lithium-ion cells – further testing

Conductive solution	Water conductivity (mS/cm)	Electrolyte concentration (g/L)	Solution conductivity (mS/cm)	Original pH
Sodium bicarbonate 53.5 mS/cm tap water	0.332	125.0	53.6	8.42
Sodium bicarbonate 53.5 mS/cm “dirty” water	1.047	125.0	53.4	8.75
Sodium chloride 53.5 mS/cm tap water	0.3265	32.5	53.5	8.1
Sodium chloride 53.5 mS/cm “dirty” water	1.047	32.7	53.5	8.2
Sodium chloride 2X salinity tap water	0.3265	70.0	107.3	7.97
Sodium chloride 2X salinity “dirty” water	1.047	70.0	107.4	7.96

7 days immersion

Lithium-ion cells – further testing

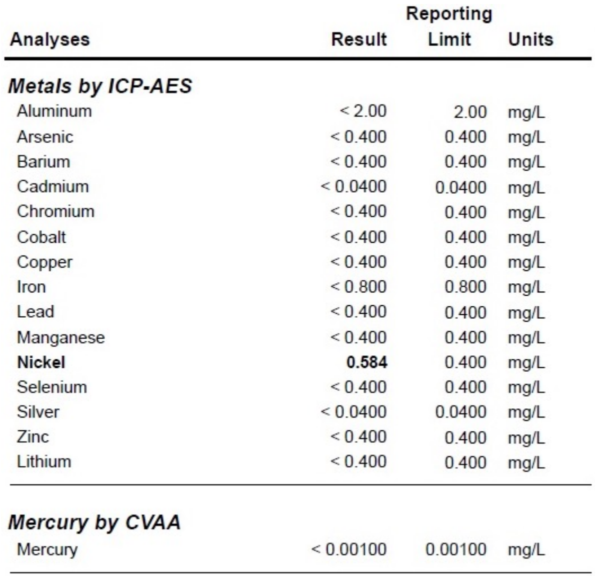


Note: 18650 cells from a different manufacturer

- The voltages of the sodium chloride solutions dropped quickly; may be linked to electrode dissolution rather than internal voltage
- The voltage in the sodium bicarbonate – “Dirty” water solution dropped suddenly after 0.97 days; electrode dissolution
- Sodium bicarbonate – Tap water: 0% SoC after 1.1 days

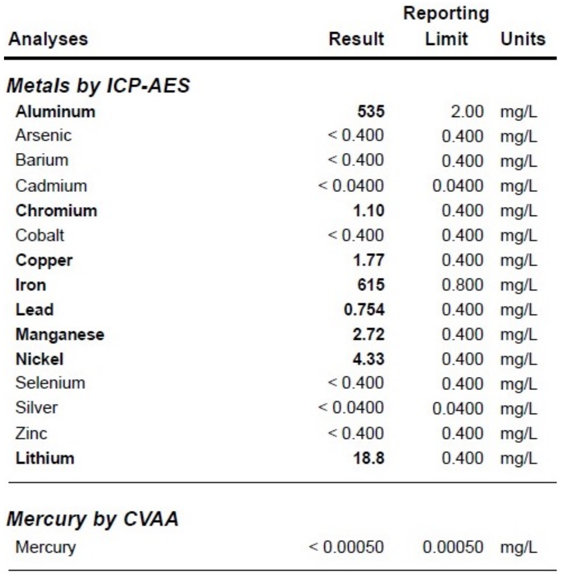
Lithium-ion cells – chemical evaluation after cell discharge

Sodium bicarbonate solution



Analyses	Result	Reporting Limit	Units
Metals by ICP-AES			
Aluminum	< 2.00	2.00	mg/L
Arsenic	< 0.400	0.400	mg/L
Barium	< 0.400	0.400	mg/L
Cadmium	< 0.0400	0.0400	mg/L
Chromium	< 0.400	0.400	mg/L
Cobalt	< 0.400	0.400	mg/L
Copper	< 0.400	0.400	mg/L
Iron	< 0.800	0.800	mg/L
Lead	< 0.400	0.400	mg/L
Manganese	< 0.400	0.400	mg/L
Nickel	**0.584**	0.400	mg/L
Selenium	< 0.400	0.400	mg/L
Silver	< 0.0400	0.0400	mg/L
Zinc	< 0.400	0.400	mg/L
Lithium	< 0.400	0.400	mg/L
Mercury by CVAA			
Mercury	< 0.00100	0.00100	mg/L

Sodium chloride solution



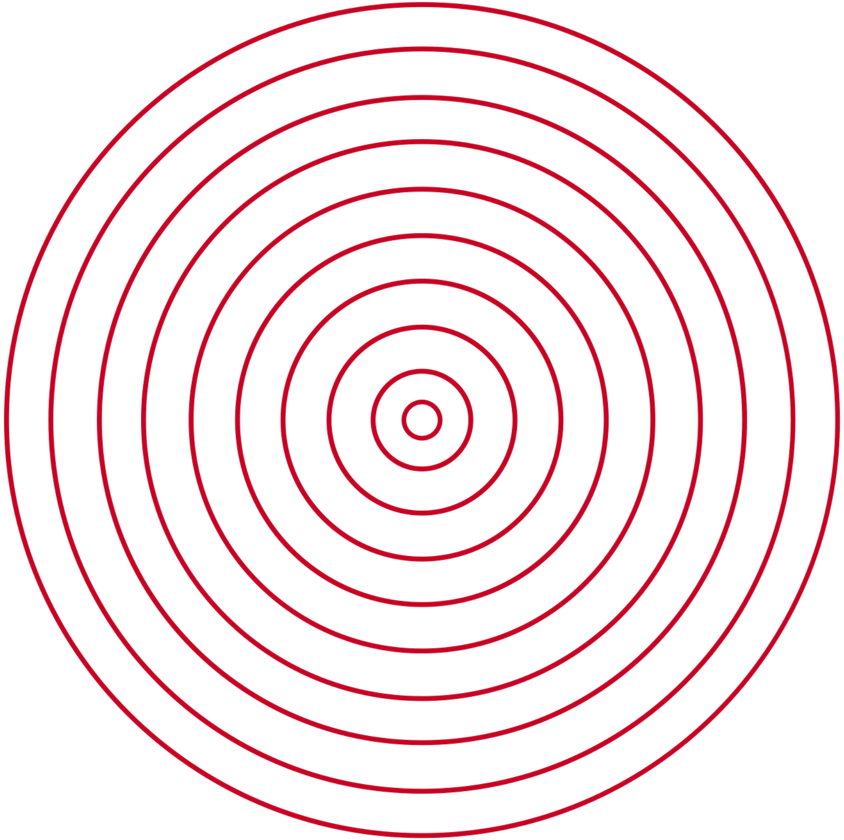
Analyses	Result	Reporting Limit	Units
Metals by ICP-AES			
Aluminum	**535**	2.00	mg/L
Arsenic	< 0.400	0.400	mg/L
Barium	< 0.400	0.400	mg/L
Cadmium	< 0.0400	0.0400	mg/L
Chromium	**1.10**	0.400	mg/L
Cobalt	< 0.400	0.400	mg/L
Copper	**1.77**	0.400	mg/L
Iron	**615**	0.800	mg/L
Lead	**0.754**	0.400	mg/L
Manganese	**2.72**	0.400	mg/L
Nickel	**4.33**	0.400	mg/L
Selenium	< 0.400	0.400	mg/L
Silver	< 0.0400	0.0400	mg/L
Zinc	< 0.400	0.400	mg/L
Lithium	**18.8**	0.400	mg/L
Mercury by CVAA			
Mercury	< 0.00050	0.00050	mg/L

- Sodium bicarbonate shows little to no dissolution
- Sodium chloride shows more dissolution of cell and indicates cell case has been breached – lithium indicates internal components

Conclusions and recommendations from research

- A sodium bicarbonate solution is a better candidate than a sodium chloride solution for immersion discharging to deter cell dissolution
    - Lowest mass loss in tests on electrodes compared to other conductive solutions
    - Chemical evaluation after discharging cells showed little to no dissolution; however, sodium chloride solution showed increased dissolution and indicated the cell case was breached
- Use municipal water rather than an unknown quality water source (i.e., pond water) to prepare the sodium bicarbonate solution
    - Have chemical analysis performed on sample of solution after immersion discharging before its disposal
- Use >78 g/L sodium bicarbonate
    - Produces minimum 50 mS/cm conductivity
    - Do not need solubility limit of sodium bicarbonate; the 53.5 mS/cm attainable does not provide notable improvement in discharge rate

Questions?



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