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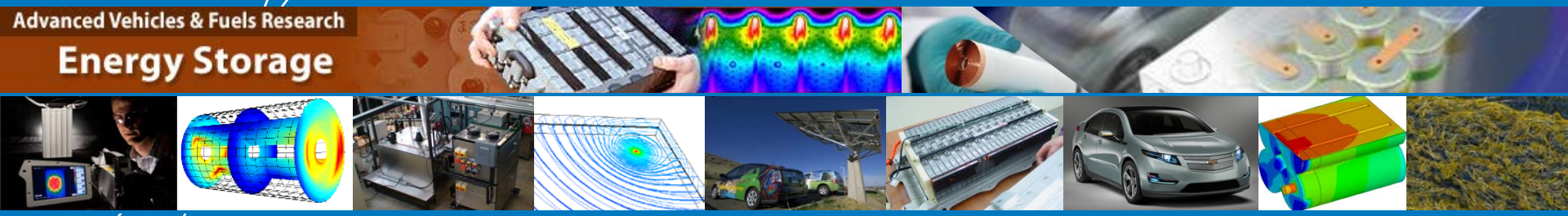
Towards the Development of Liquid Organic Redox Systems for Flexible Energy Storage



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http://www.nrel.gov/vehiclesandfuels/energystorage/

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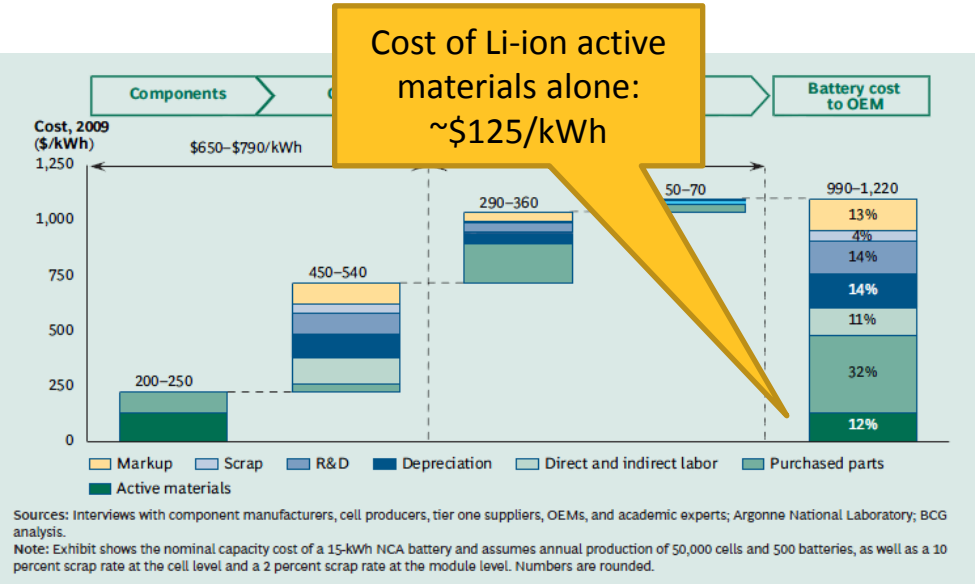
Motivation: Material Supply

- To be adopted by the mass market, cost needs to be extremely low and required materials must be abundant
- Domestically sourced materials would help the US reach its energy security goals



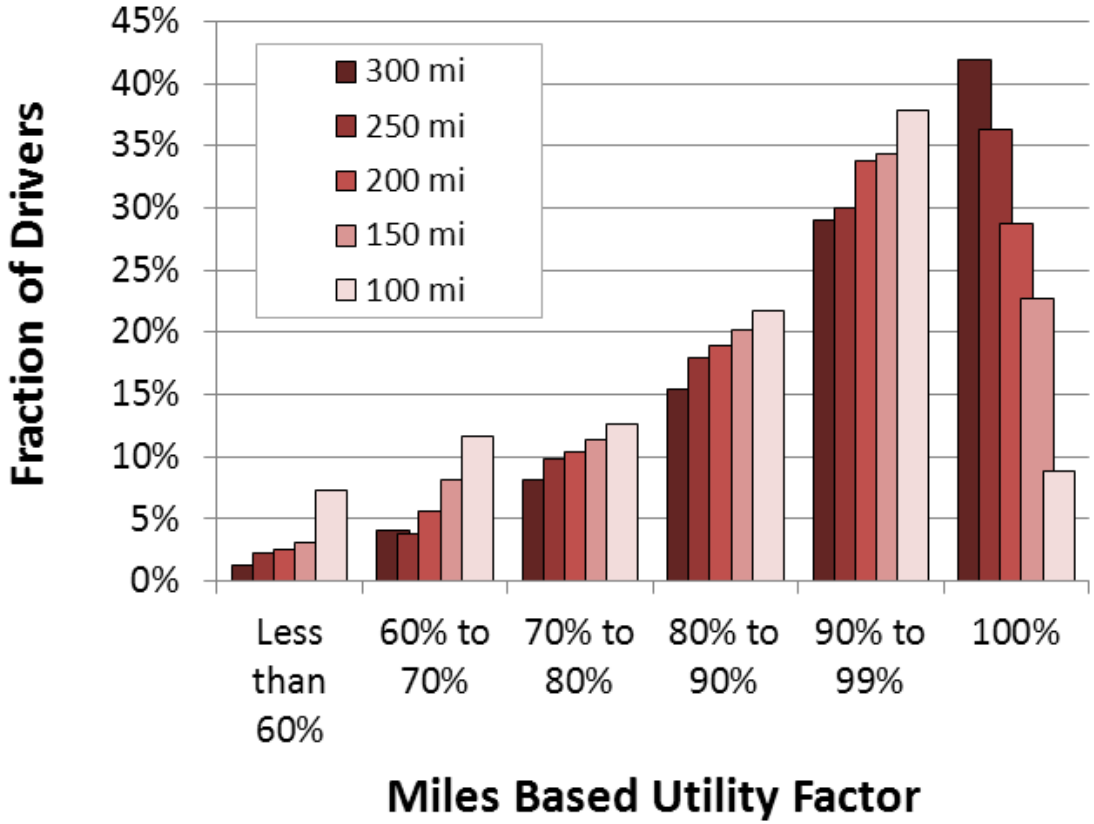
Source: Boston Consulting Group

Cost target for a transformational BEV:
$100/kWh

250 Wh/kg
400 Wh/l
$125/kWh

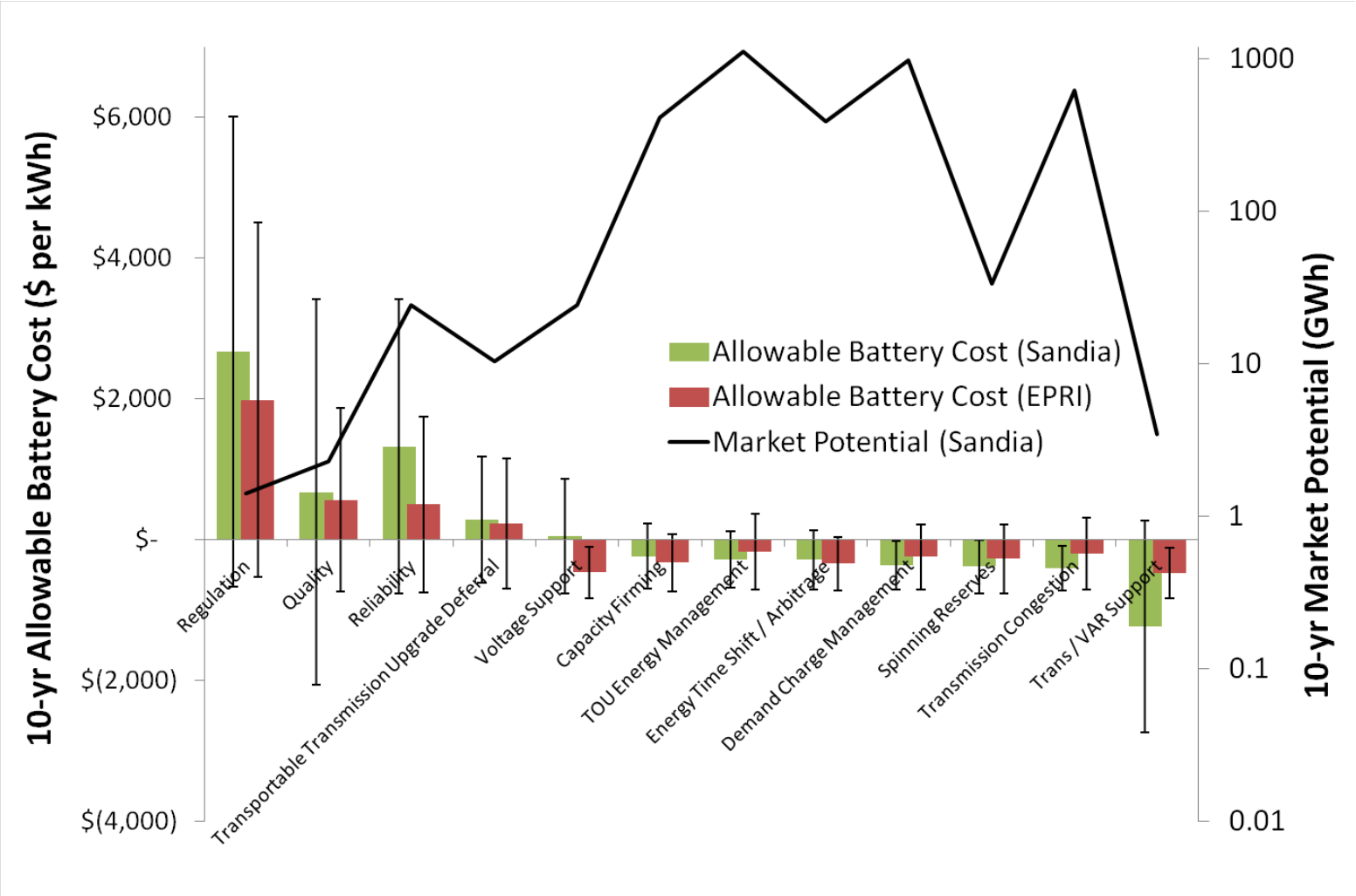
Motivation: Consumer Drive Patterns

- A 100 mile range BEV charged at home can satisfy a large portion of many consumers' driving needs
- In most cases, the remaining unachievable travel occurs in long trips and tours. These would require a BEV with quick-charging or battery swapping capability
- High energy density and quick-charging capability are often mutually exclusive characteristics in traditional battery technology
- Full battery swapping strategies are challenged by economics, consumer acceptance, and vehicle OEM compliance



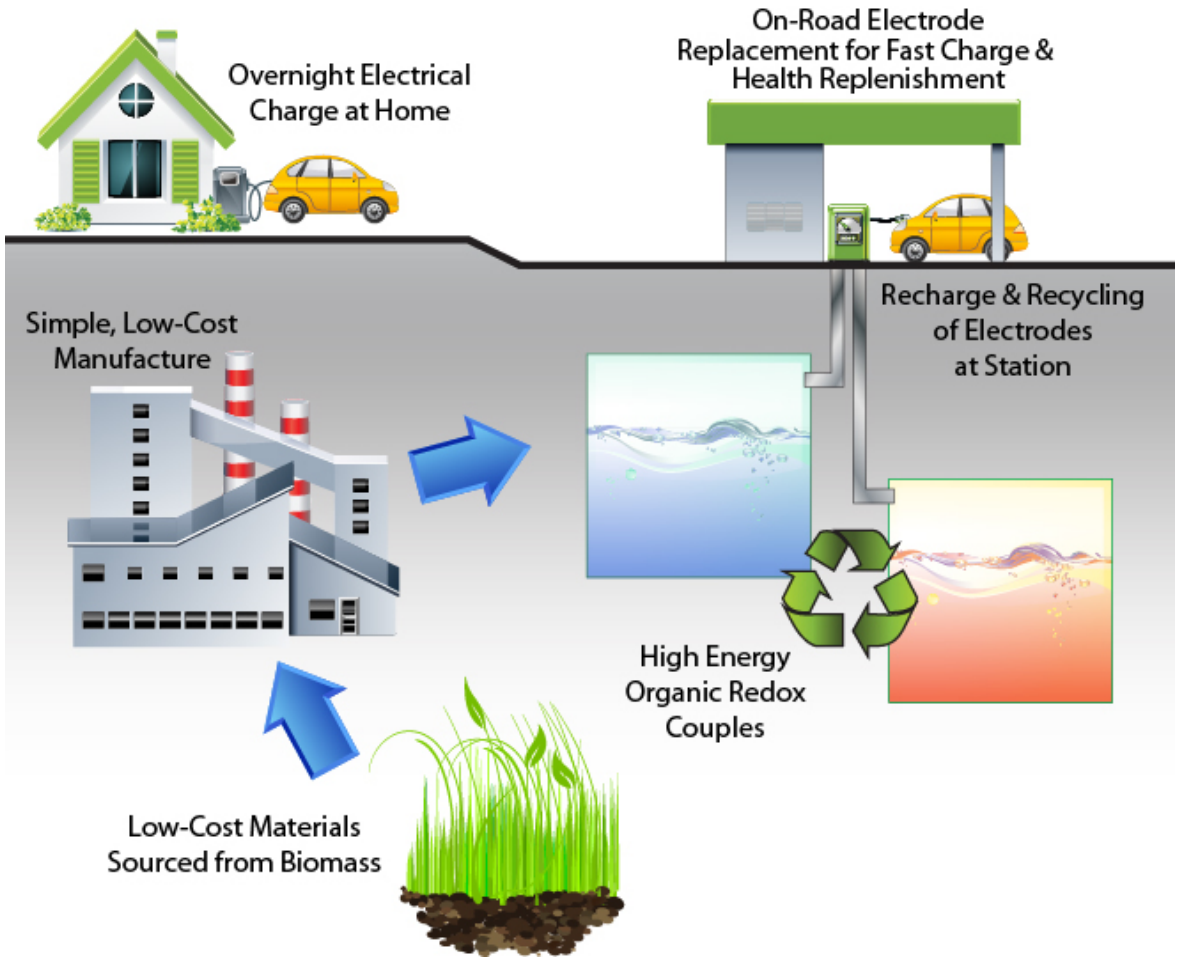
Histogram of miles-based individual vehicle utility factors for BEVs of multiple ranges based upon Travel Choices Study data shows even 300 mile BEVs need quick-charging to meet the needs of many drivers

Motivation: Stationary Storage



- **Most applications are only viable under very optimistic sets of assumptions**
- **Most profitable markets have small potentials**

Vision



- **Slow electrical recharge at home enables the majority of driving miles**
- **Liquid anolyte and catholyte to facilitate quick mechanical recharge & health replenishment**
  - Liquid systems can enable safety and cost improvements, too
- **Organic chemistries can meet all of the necessary material supply criteria (sustainable, domestic, low-cost), but can they provide adequate performance?**

Approach

- **Chemistry Database:** Shortlist from industrially viable baseline molecules and conduct screening tests on a large range of organic redox compounds and solvents to down-select viable candidates.

- **Structural Study:** Develop computational tools to compute nature of redox reaction, structural stability during cycling, and impact of substitutions on redox potentials and solubility.

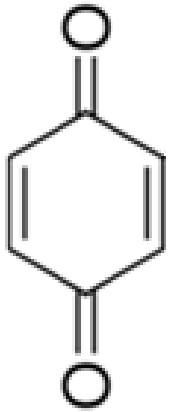
- **Bulk Electrolysis:** Develop a cell for bulk electrolysis testing of compounds. Apply to validate computational methods and further down-select high performance candidates.

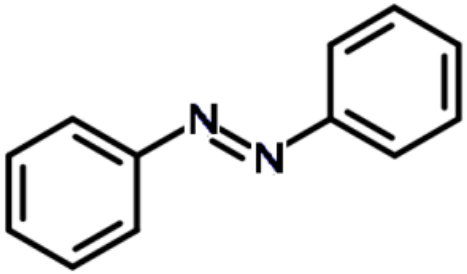
Chemistry Database

- Compiled a list of hundreds of organic redox compound reactions with data on molecular weight, number of electrons transferred, redox potential , cost, NFPA ratings, and other info available from NREL's biomass database with extensive input from the industry.
- Compiled a list of dozens of organic solvents with data on density, cost, melting, boiling, and flash points, viscosity, dielectric constant, NFPA ratings, and other info available from literature.
- Performed screening tests of select compounds and solvents in the lab (e.g. cyclic voltammetry, solubility, solvent stability, conductivity, etc.)
- Developed a screening tool and down-selected top anodes, cathodes, and solvents based on projected cell-level performance, cost, and other metrics.

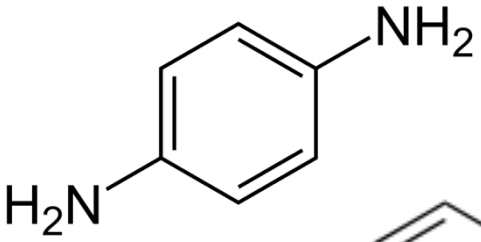
Compound Family Selection

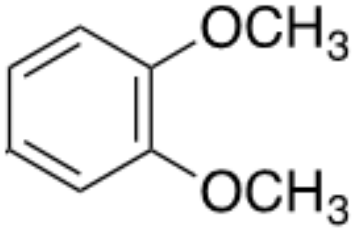
- **Anodes**
  - Azobenzene: 1 e-, ~1.75M, and ~0.7V, but only reversible in AcN
  - Benzoquinones: 2 e-, 0.5 to 4.3M and 1.0 to 2.3 V, lots of literature





- **Cathodes**
  - Phenylenediamine: 2 e-, 3.3 to 4.9M, and ~3.2V; ease of manufacture.
  - Substituted Dimethoxy Benzenes: 1 e-, 6 to 7M, and 4.2V; very high solubility



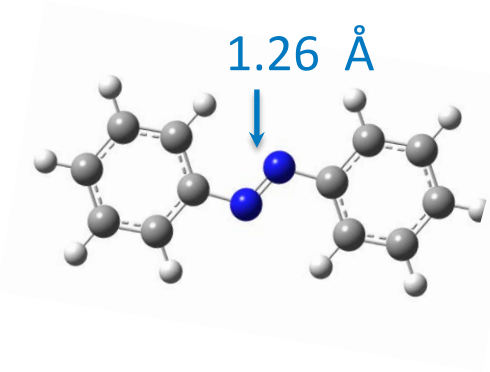


Predicting Reversibility

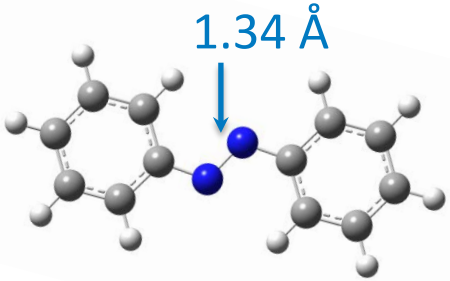
- **DFT tools developed and applied to assess bond length changes in neutral and reduced (oxidized) species. Excessive changes imply bond breaking.**

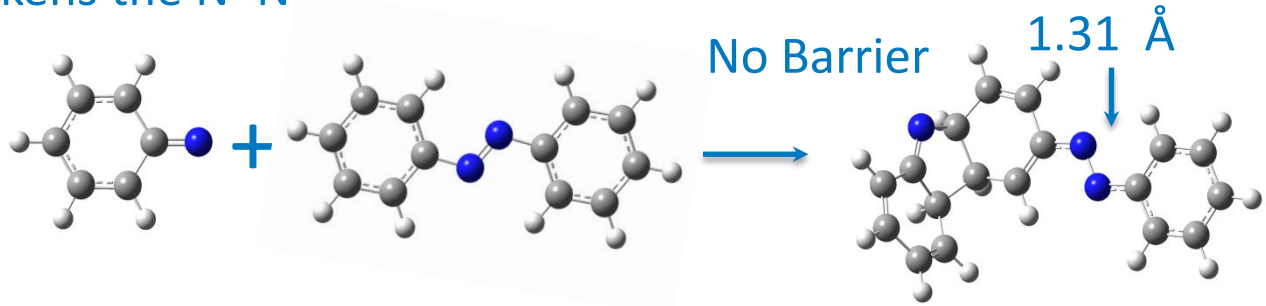
- **E.g., Azobenzene:**
- Reduction results in increased bond length between two Nitrogens
- The resulting radical anion can nonselectively attack another azobenzene. The electron localizes on and weakens the N–N bond.

Neutral



Reduced



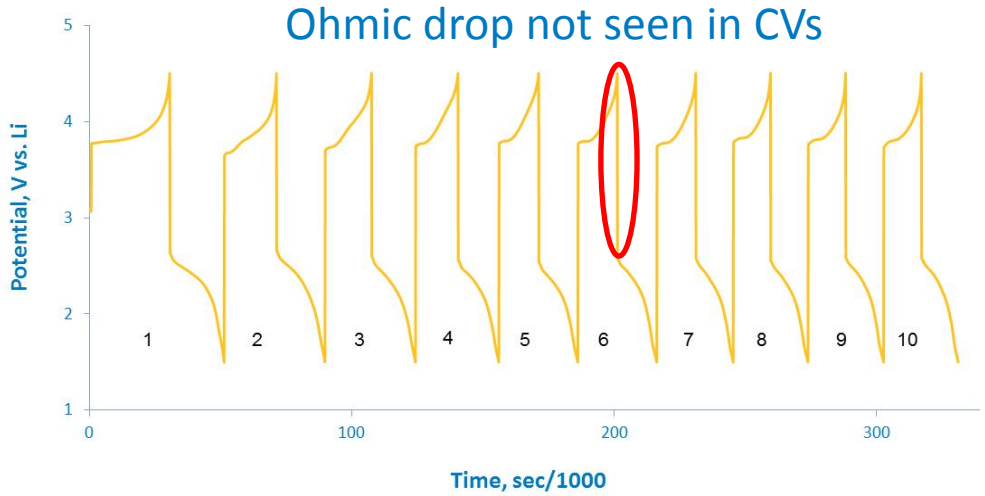


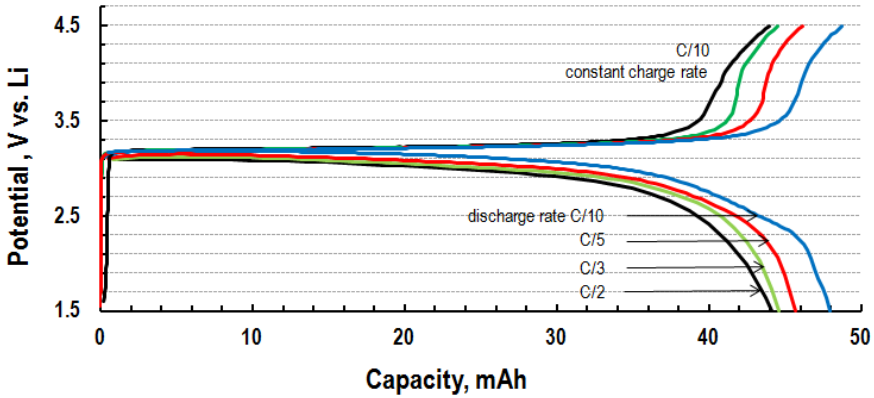
Bulk Electrolysis Cell Development

- **New System; newer challenges**
  - Sealing: O-ring design/selection for chemical and mechanical compatibility with solvents and ceramic separators
  - Separators: ionic conductivity, mechanical stability, **organic surface deposits**, chemical compatibility, diffusion, voltage stability
  - Current Collectors: resistance effects, compatibility with salts, **eliminating reductive/oxidative effects**

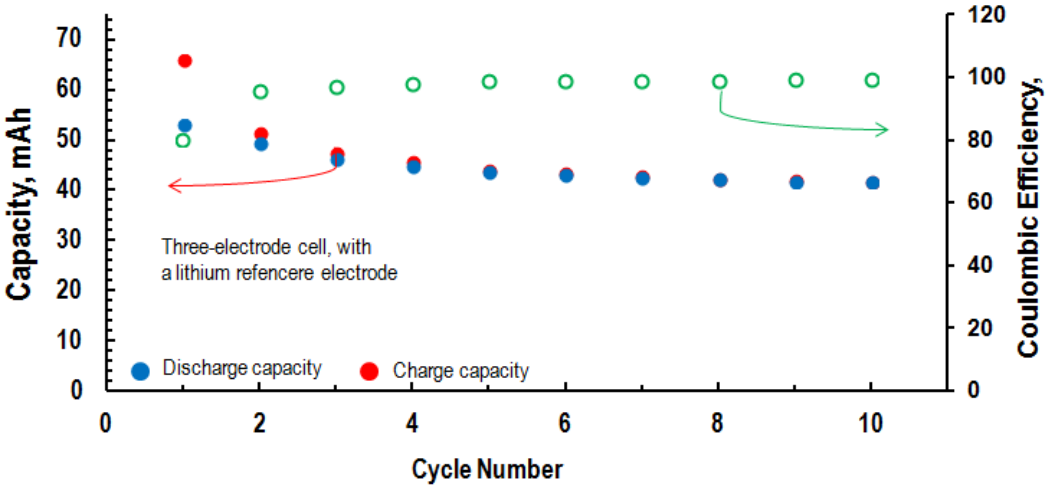
Bulk Electrolysis Results

Ohmic drop not seen in CVs



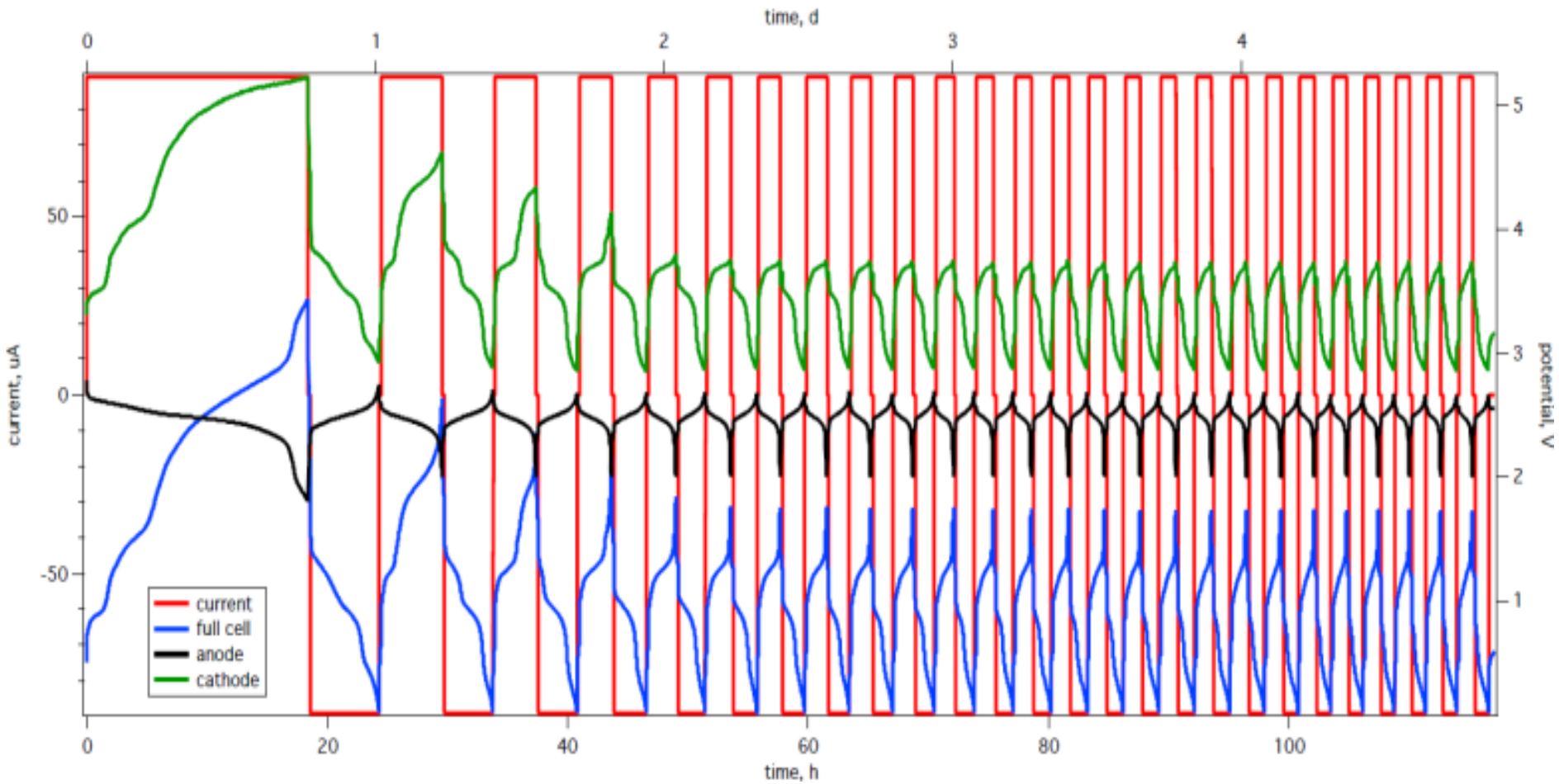


80.3% of theoretical capacity observed at C/2



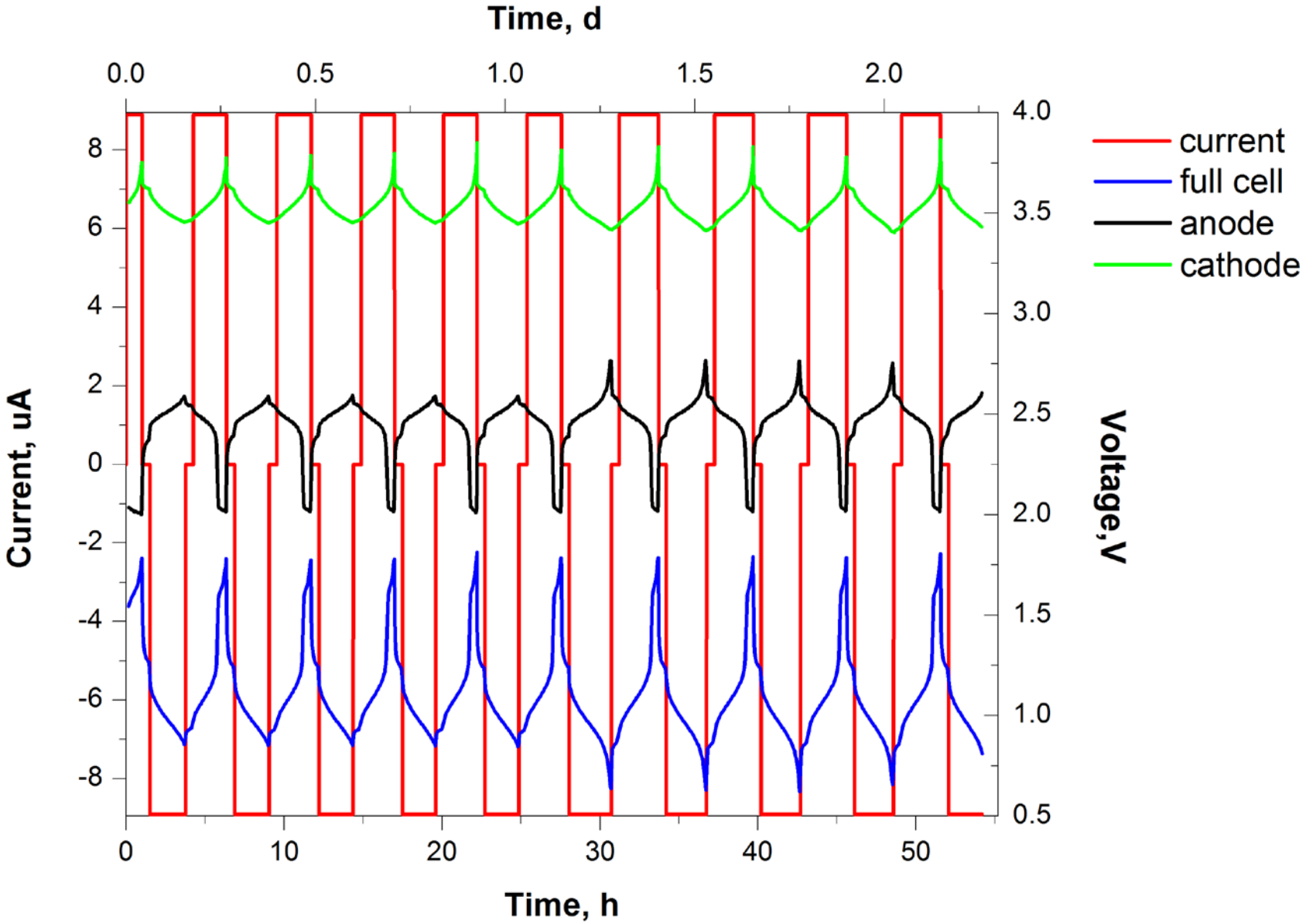
Good rate capability over the range measured (C/10 – C/2)

Full-Cell Cycling Results: Gen1



- Initial few cycles showing some irreversible loss
- Possibly due to high local over-potentials on the surface of the membrane

Full-Cell Cycling Results: Gen 2



Summary

Status to-date

- Demonstrated reversible chemistries in bulk-electrolysis set-up (cycling efficiencies around 90%)
- No optimization of the cell was performed – higher concentration of active material requires lower membrane resistivity
- Measured energy density ~ 30 Wh/kg and Specific energy ~50 Wh/l when using 0.2 M solutions (Solubility limits are ~ 2.2M)
- Projected energy density: ~ 330 Wh/kg
  Projected specific energy: ~ 550 Wh/l
  based on linear extrapolation of test results

Next Steps

- Resolve membrane resistivity issues
- Improve solubility of salts in active material and operating voltage window
- Enhanced visualization tools to better interpret structure-property relationships
- Demonstrate performance at scale

Acknowledgements

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