## Dissecting the quinone bromide flow battery

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Dissecting the Quinone Bromide Flow Battery

Qing Chen, Michael R. Gerhardt, Louise Eisenach, Michael P Marshak, Roy G Gordon, Michael J Aziz.

5-26-2015
Quinone-bromide flow battery

References:
QBFB reaches 1.0 W/cm²

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Membrane</th>
<th>Flow rate</th>
<th>Temperature</th>
<th>Posolyte</th>
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</thead>
<tbody>
<tr>
<td>Baked SGL 10AA</td>
<td>Pretreated 212</td>
<td>200 mL/min</td>
<td>20 °C</td>
<td>3 M HBr, 0.5 M Br₂</td>
</tr>
<tr>
<td>SGL 10AA</td>
<td>212</td>
<td>100 mL/min</td>
<td>30 °C</td>
<td>3.5 M HBr, 0.5 M Br₂</td>
</tr>
<tr>
<td>Etched Toray 060</td>
<td>115</td>
<td>50 mL/min</td>
<td>40 °C</td>
<td>2.5 M HBr, 0.5 M Br₂</td>
</tr>
</tbody>
</table>

When kinetics and mass transport limits are insignificant, polarization curves are linear.
Ohmic resistors in the cell

Cell Discharge

H₂AQDS → e⁻ → H⁺ → e⁻ → Br⁻ → Br₂

Ionic resistance
Electrolyte +
Electrolyte –
Membrane

Faradaic resistance

Electronic resistance

We may use linearized Butler-Volmer
Separating voltage losses

Full Cell

50% SOC
Discharge
Base case

Cell Voltage (V)

50% SOC
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.0 0.2 0.4 0.6 0.8 1.0

Current density (A/cm²)

325 mΩ cm²

104 mΩ cm²

Membrane ionic + electronic (+ & -)

Membrane ionic: 60 mΩ cm²

Electronic: 22 mΩ cm² (each)

EIS
50% SOC
0 A DC current
0.01 A AC current

Z_{\text{img}} (\Omega \text{ cm}^2)

Z_{\text{real}} (\Omega \text{ cm}^2)

H_2AQDS
Nafion
Br₂

AQDS
H₂⁺
Br⁻
e⁻

Flow Plate

Flow Plate

104 mΩ cm²
Separating voltage losses

Membrane ionic + Electronic (+ & -) 104 mΩ cm²

Electrolyte ionic (+) + Faradaic (+) 94 mΩ cm²

Electrolyte ionic (-) + Faradaic (-) 127 mΩ cm²

< 10 mΩ cm²

Membrane ionic + Electronic (+ & -) 104 mΩ cm²

50% SOC
H₂AQDS oxidation
Base case

Pd-H RE (~50 mV vs. RHE)

Nafion

H₂AQDS

Flow Plate

Counter side

Neg. side

Full Cell

50% SOC
Discharge
Base case

Cell Voltage (V)

Current density (A/cm²)

0.0 0.2 0.4 0.6 0.8 1.0

0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45

0.0 0.2 0.4 0.6 0.8 1.0

0.40
0.35
0.30
0.25
0.20
0.15

0.15
0.20
0.25
0.30
0.35
0.40

0.15
0.20
0.25
0.30
0.35
0.40

0.0 0.2 0.4 0.6 0.8 1.0

272 mΩ cm²

127 mΩ cm²

145 mΩ cm²

Membrane ionic + Electronic (-)
Two phase conducting and Current distribution

1D homogeneous porous electrode model neglecting mass transport

Electronic current, $i_s$

Faradaic current, $i_f$

Ionic current, $i_l$

$\phi_1$

$\phi_2$

$\rho_s$

$\rho_f$

$\rho_l$

$s$: solid electrode phase; $l$: liquid electrolyte phase; $f$: Faradaic

$\rho$: resistivity; $\Phi$: potential; $i$: current density; $\Phi$: voltage;

$\eta$: overvoltage; $L$: electrode thickness

Overvoltage $\eta_{neg0} = \phi_1 - \phi_2 \approx \int_0^L i_l(x) \rho_l \, dx$

Resistance $r_{neg0} = \frac{\eta_{neg0}}{i_{tot}} = \rho_l \int_0^L \frac{i_l(x)}{i_{tot}} \, dx$

$i_{tot} = i_s + i_l$

$i_s = \nabla \phi_s / \rho_s$

$i_l = \nabla \phi_l / \rho_l$

$i_f \propto \nabla \cdot i_s = f[\phi_s - \phi_l]$

Reference

Potential probes for current distribution

Neg. polarization vs. Pd-H

Solid phase voltage

\[ i_s = \frac{V_{1, 2, 3}}{r_{1, 2, 3}} \]

All \( i_s / i_{tot} \) appear independent of \( i_{tot} \)
Overvoltage from the negative side

\[ r_{\text{nego}} = \frac{\eta_{\text{nego}}}{i_{\text{tot}}} = \rho_l \int_0^L \frac{i_l(x)}{i_{\text{tot}}} \, dx \]

Line & scatters: experimental values
Dashed lines: 1D porous electrode model

Neg. \( \rho_l \sim 2.2 \, \Omega \text{ cm} \)
(~ 5.4 \( \Omega \text{ cm} \) after Bruggerman correction using 55% porosity)

161 \( \text{m\Omega cm}^2 \)

Electronic + Electrolyte Ionic + Faradaic

All \( i_s/i_{\text{tot}} \) appear independent of \( i_{\text{tot}} \)
Conclusions

• Highest QBFB peak power density to date: 1.0 W/cm²
• Linear polarization for QBFB
• Contributions to overvoltage have been quantified
• Negative Faradaic reaction occurs primarily in the first 300 µm of the electrode
• Enables future engineering improvements

Acknowledgements
We thank the Alán Aspuru-Guzik research group for molecule property theoretical calculation, Sustainable Innovations, LLC. for Product-to-Market insights and ARPA-E for funding the research.

Thank you!
Capacity loss $\eta_i$-loss
- Quinone decomposition
- Negolyte leakage

Latent-$\eta_i$-loss
- Cell resistance change
- Water transport

Non-Capacity-loss $\eta_i$-loss
- $Br_2$ crossover
- $H_2$ evolution
- $O_2$ permeation

Minority side leakage & active species decomposition

Posolyte leakage
- Posolyte decomposition
- Posolyte crossover
- $CO_2$ & $O_2$ evolution

Majority side leakage, decomposition & side-reactions

Minority side side-reactions
EIS
50% SOC
0 A DC current
0.01 A AC current

\[ Z_{\text{img}} (\Omega \text{ cm}^2) \]

\[ Z_{\text{real}} (\Omega \text{ cm}^2) \]
Fig. 5. The potential profile and current distribution for symmetric electrodes geometry under secondary current distribution (Wa (anode) = 0.1, Wa (cathode) = 100).