Quinone electrochemistry in acidic and alkaline solutions and its application in large scale energy storage

The Harvard community has made this article openly available. Please share how this access benefits you. Your story matters

Citation

Citable link
http://nrs.harvard.edu/urn-3:HUL.InstRepos:34325476

Terms of Use
This article was downloaded from Harvard University’s DASH repository, and is made available under the terms and conditions applicable to Open Access Policy Articles, as set forth at http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#OAP
Quinone electrochemistry in acidic and alkaline solutions & its application in large scale energy storage

Michael R. Gerhardt¹, Kaixiang Lin², Qing Chen¹, Michael P. Marshak¹,³, Liuchuan Tong², Roy G. Gordon¹,², Michael J. Aziz¹
1) Harvard School of Engineering and Applied Sciences, Cambridge, MA 02138
2) Department of Chemistry and Chemical Biology, Harvard University, Cambridge MA 02138
3) Department of Chemistry and Biochemistry, University of Colorado, Boulder CO 80309
Flow Batteries Store Energy

Energy Storage (kWh)

Power Generation (kW)

Photo: Eliza Grinnell, SEAS Communications
Quinones are Cheap, Versatile, & Robust

In aqueous acidic solution

Quinones are Cheap, Versatile, & Robust

\[
\text{Quinone} + 2H^+ + 2e^- \leftrightarrow \text{Quinone-Hydroxide}
\]

In aqueous acidic solution

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Solution Cost ($/kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quinone-Bromide</td>
<td>&lt;$27</td>
</tr>
<tr>
<td>Vanadium Redox</td>
<td>$50 – $180</td>
</tr>
</tbody>
</table>

"I wish I could get that price!"

Quinones are Cheap, Versatile, & Robust

In aqueous acidic solution

Chemistry | Solution Cost ($/kWh)
---|---
Quinone-Bromide | <$27
Vanadium Redox | $50 – $180

“I wish I could get that price!”

Quinones are Cheap, Versatile, & Robust

"I wish I could get that price!"

Chemistry | Solution Cost ($/kWh)
--- | ---
Quinone-Bromide | <$27
Vanadium Redox | $50 – $180

Chemistry Solution Cost ($/kWh)

Quinone-Bromide | <$27
Vanadium Redox | $50 – $180

AQDS redox is reversible

AQDS redox is reversible

Reversible 2-electron model: assume AQDS concentration at electrode surface is dictated by Nernst equation [1]. Reaction rate is mass transport limited.

Measured rate constant $k_0 = 7.2 \times 10^{-3}$ cm/s [2]

\[ E_0 = 0.210 \text{ V vs SHE} \]

---

The Quinone – Bromine Flow Battery

No catalyst required

High Power Operation with AQDS/HBr battery

Data: Qing Chen
Glassy carbon electrode, 3 mm dia, 25 mV/s scan rate, 25 °C. Ag/AgCl reference.
Pt coil counter electrode. Supporting electrolyte 1 M H₂SO₄
Quinone concentration 1 mM
Glassy carbon electrode, 3 mm dia, 25 mV/s scan rate, 25 °C. Ag/AgCl reference.
Pt coil counter electrode. Supporting electrolyte 1 M H₂SO₄
Quinone concentration 1 mM
Glassy carbon electrode, 3 mm dia, 25 mV/s scan rate, 25 °C. Ag/AgCl reference. Pt coil counter electrode. Supporting electrolyte 1 M H$_2$SO$_4$. Quinone concentration 1 mM.
Posolyte: 0.5 M Br₂, 3 M HBr
Negolyte: 1 M quinone, 1 to 2 M H₂SO₄ (3 M total proton concentration)
Increase Cell Voltage by Modifying Molecules

Posolyte: 0.5 M Br₂, 3 M HBr
Negolyte: 1 M quinone, 1 to 2 M H₂SO₄ (3 M total proton concentration)
Reversible 2-electron model: assume AQS concentration at electrode surface is dictated by Nernst equation [1]. Reaction rate is mass transport limited.

**Quasireversible model**: Assume Butler-Volmer kinetics with a rate constant $k_0 = 2 \times 10^{-3} \text{ cm/s}$ [1].

Switching Molecules Leads to Higher Power

Voltage (V) vs. Current Density (A/cm²)

- Charge
- Discharge

- AQS
- AQDS

Posolyte: 0.5 M Br₂, 3 M HBr
Switching Molecules Leads to Higher Power

![Diagram showing power density vs. current density for AQS and AQDS at 90% and 50% SoC.]

- **Posolyte:** 0.5 M Br₂, 3 M HBr
pH affects AQDS electrochemistry

\[ AQ + (N_{H^+})H^+ + (N_{e^-})e^- \rightarrow H(N_{H^+})AQ^{\pm z} \]
pH affects AQDS electrochemistry

\[ AQ + (N_{H^+})H^+ + (N_{e^-})e^- \rightarrow H(N_{H^+})AQ^{\pm z} \]

\[ E = E^{0'} + \frac{RT}{(N_{e^-})F} \ln \left( \frac{[AQ][H^+]^{N_{H^+}}}{[H_mAQ^{\pm z}]} \right) \]
pH affects AQDS electrochemistry

\[ AQ + (N_{H^+})H^+ + (N_{e^-})e^- \rightarrow H(N_{H^+})AQ^{\pm z} \]

\[ E = E^0' + \frac{RT}{(N_{e^-})F} \ln \left( \frac{[AQ][H^+]^{N_{H^+}}}{[H_mAQ^{\pm z}]} \right) \]

\[ E = E^0' - \frac{RT}{F} \left( \frac{N_{H^+}}{N_{e^-}} \right) (pH) + C \]
pH affects AQDS electrochemistry

\[ E = E^0' - \frac{RT}{F} \left( \frac{N_{H^+}}{N_{e^-}} \right) (pH) + C \]
**pH affects AQDS electrochemistry**

- **pKa$_1$ = 7.70,**
- **pKa$_2$ = 10.52**
- **E$_0$ = 0.229 V**
- **E$_0$$_{dianion}$ = −0.313 V**
pH affects AQDS electrochemistry

$E^0 = 0.229 \text{ V}$

$pK_{a1} = 7.70,$

$pK_{a2} = 10.52$

$E^0_{\text{dianion}} = -0.313 \text{ V}$
pH affects AQDS electrochemistry

\[ E^0 = 0.229 \text{ V} \]

\[ E^0_{\text{dianion}} = -0.313 \text{ V} \]

pKa\(_1\) = 7.70,

pKa\(_2\) = 10.52
Glassy carbon electrode, 3 mm dia, 50 mV/s scan rate, 25 °C. Ag/AgCl reference. Pt coil counter electrode. Supporting electrolyte H₂SO₄ or KOH. Quinone concentration 1 mM
AQDS reduction kinetics as function of pH

Glassy carbon electrode, 3 mm dia, 50 mV/s scan rate, 25 °C. Ag/AgCl reference. Pt coil counter electrode. Supporting electrolyte H₂SO₄ or KOH. Quinone concentration 1 mM
AQDS reduction kinetics as function of pH

Glassy carbon electrode, 3 mm dia, 50 mV/s scan rate, 25 °C. Ag/AgCl reference. Pt coil counter electrode. Supporting electrolyte H₂SO₄ or KOH. Quinone concentration 1 mM.
Optimizing molecule for basic solutions
Optimizing molecule for basic solutions

2,6-dihydroxy 9,10-anthraquinone (2,6-DHAQ)

pH 14

Current Density (mA/cm²)

Potential (V vs SHE)
Two-electron transfer model can’t explain CV

Current Density (mA/cm$^2$)

Overpotential (V)

2,6-DHAQ

Model

$k_0 = 1 \times 10^{-2}$ cm/s

OH

O

HO

O

OH

HO
Two-electron transfer model can’t explain CV

Current Density (mA/cm$^2$)

Overpotential (V)

$\text{2,6-DHAQ}$

Model

$k_0 = 1 \times 10^{-3}$ cm/s
Two-electron transfer model can’t explain CV

Current Density (mA/cm$^2$) vs. Overpotential (V)

2,6-DHAQ
Model

$k_0 = 1 \times 10^{-4}$ cm/s
Sequential 1 e⁻ transfers could explain CV

![Graph showing current density vs. overpotential for 2,6-DHAQ](image-url)
Sequential 1 e\textsuperscript{−} transfers could explain CV

Current Density (mA/cm\textsuperscript{2})

Overpotential (V)

E\textsubscript{0,1} = -0.657 vs SHE

k\textsubscript{0,1} = 7 \times 10^{-3} \text{ cm/s}
Sequential 1 e⁻ transfers could explain CV

Current Density (mA/cm²) vs Overpotential (V)

- 2,6-DHAQ
- Model $i_1$
- Model $i_2$

$E_{0,1} = -0.657$ vs SHE
$k_{0,1} = 7 \times 10^{-3}$ cm/s
$E_{0,2} = -0.717$ vs SHE
$k_{0,2} = 7 \times 10^{-3}$ cm/s
Sequential 1 e⁻ transfers could explain CV

![Graph showing current density vs overpotential for different models and a chemical structure.]

- **2,6-DHAQ**
- **Model i₁**
- **Model i₂**
- **Model i₁ + i₂**

- $E_{0,1} = -0.657$ vs SHE
- $k_{0,1} = 7 \times 10^{-3}$ cm/s
- $E_{0,2} = -0.717$ vs SHE
- $k_{0,2} = 7 \times 10^{-3}$ cm/s
Quinone – Ferrocyanide Flow Battery

Figure by Kaixiang Lin, manuscript under review
Cyclic voltammogram of 4 mM 2,6-DHAQ (dark cyan curve) and ferrocyanide (gold curve) scanned at 100 mV/s

Work performed by Kaixiang Lin, manuscript under review
Strategies for Increasing Cell Voltage

Use functional groups to create more reducing quinones

![Graph showing current density vs. potential for AQDS, AQS, and DHAQDS]

Chemical structures of AQDS, AQS, and DHAQDS
Use functional groups to create more reducing quinones

Use quinones in alkaline environment

\[
\text{AQDS} \quad \text{AQS} \quad \text{DHAQDS}
\]

\[
\begin{align*}
\text{E}^0 (\text{mV vs. SHE}) & = -0.1E + 0.592 \\
\text{pH} & = 0.1 \times \text{Current Density} \times 2 \\
\end{align*}
\]
Use functional groups to create more reducing quinones

Use quinones in alkaline environment

**ENFL 403**: Organic Aqueous Redox Flow Batteries
Prof. Michael J. Aziz
Thursday, August 20, 1:35 pm Room 258B
This work was partially funded through the US Department of Energy ARPA-E Award DE-AR0000348 and partially funded through the Harvard School of Engineering and Applied Sciences.

Top to bottom, left to right:
Drew Wong, Prof. Mauricio Salles, Alvaro Valle, Dr. Junling Huang
Dhruv Pillai, Prof. Michael Marshak, Dr. Rafa Gómez-Bombarelli, Liuchuan Tong
Lauren Hartle, Dr. Sungjin “James” Kim, Dr. Changwon Suh,
Kaixiang Lin, Michael Gerhardt, Dr. Eugene Beh
Dr. Qing Chen, Louise Eisenach, Jennifer Wei
Prof. Michael Aziz, Prof. Roy Gordon, Prof. Alán Aspuru-Guzik
Assumptions for reversible case

- Linear, planar diffusion
  \[ - \frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2} \]
- Initial conditions:
  - \( C_O(x, t = 0) = C_O^* \), \( C_R(x, t = 0) = 0 \)
- Boundary conditions:
  - \( C_O(x \to \infty, t) = C_O^* \)
- All current is diffusion controlled
  \[ - i(t) = nFAD_O \left( \frac{\partial C_O(x,t)}{\partial x} \right)_{x=0} \]
- Reversible reaction. Nernst equation applies:
  \[ - \frac{C_O(x=0,t)}{C_R(x=0,t)} = e^{\left( E_i - nF \nu - E^0 \right) / RT} \]

Notation follows Bard and Faulkner for the reaction \( O + ne \rightarrow R \).
Quasireversible Charge Transfer

- New boundary condition:

\[
\frac{i(t)}{nFAR} = D_0 \left( \frac{\partial C_O(x, t)}{\partial x} \right)_{x=0} = k_f C_O(0, t) - k_b C_R(0, t)
\]

\[
k_f = k_0 e^{\frac{-\alpha nF}{RT} (E-E^0)}, \quad k_b = k_0 e^{\frac{(1-\alpha) nF}{RT} (E-E^0)}
\]

- Define a new variable: \( \psi = \frac{\gamma^\alpha k_0}{\sqrt{\pi aD_0}} \)

\( \psi \rightarrow \infty: \) Reversible

\( \psi \rightarrow 0: \) Irreversible

\[
\frac{\chi(at)[\gamma(C_O^*/C_R^*)S(at)]^\alpha}{\psi} = 1 - S(at) - \int_0^{at} \frac{\chi(z)dz}{\sqrt{at-z}} - \gamma (C_O^*/C_R^*)S(at) \int_0^{at} \frac{\chi(z)dz}{\sqrt{at-z}}
\]

AQDS redox assuming $k_0 = 7.2 \times 10^{-3}$
$E^o = -0.83 \text{ V}$  \hspace{1cm} $E^o = 0.44 \text{ V}$

$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$  \hspace{1cm} $\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^-$

$E^o = 0 \text{ V}$  \hspace{1cm} $E^o = 1.23 \text{ V}$

$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  \hspace{1cm} $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$

1 M KOH  \hspace{1cm} 1 M H$_2$SO$_4$
The 1+1 model fails to explain AQDS redox
The 1+1 model fails to explain AQDS redox
The 1+1 model fails to explain AQDS redox
The 1+1 model fails to explain AQDS redox
The 1+1 model fails to explain AQDS redox
Aqueous quinone/hydroquinone couples exhibit rapid redox kinetics, require no electrocatalyst, and are inexpensive, making them attractive candidates for large-scale energy storage devices such as flow batteries $^{1-3}$. In acidic solutions, quinones undergo a rapid two-proton, two-electron reduction; however, in alkaline aqueous solutions, the picture is less clear$^4$. Under the right conditions, a two-electron reduction can occur as successive one-electron steps separated by a small difference in the reduction potential of each step. The underlying mechanism for the reduction of various quinones is explored as a function of pH and reduction potential. Using substituted anthraquinones and the bromine/hydrobromic acid couple, a flow battery exhibiting an open circuit voltage above 1.0 V and a peak galvanic power density above 0.7 W cm$^{-2}$ is demonstrated. Furthermore, by employing soluble metal coordination complexes, a flow battery with an open circuit voltage exceeding 1.3 V is demonstrated. Mechanisms of capacity loss during cell cycling are discussed.

Check out 2013-04-xx thru 2013-06-xx
In Half Cell Electrochemistry
Also the Pourbaix diagram origin file

1. Is concentration constant?
I think it’s a fair assumption to make. I don’t explicitly say it is anywhere and I don’t have a good record of it in my lab notebook. But my slide deck from 2013-05-23 says I was adding KOH and H2SO4 to adjust pH. Likely the volume didn’t change much so conc shouldn’t change much.

From Bard:
A case of particular interest occurs when \( \Delta E_0 = -\frac{2RT}{F} \ln 2 \sim -35.6 \text{ mV} \). This occurs when there is no interaction between the reducible groups on O, and the additional difficulty adding the extra electron arises purely from statistical (entropic) factors.
DHAQDS redox is less clear

Reversible model doesn’t quite fit
Plugging in measured $k_0$ value helps a little
Assuming a higher bulk DHAQDS concentration explains the height of the reduction peak.
Assuming more sluggish kinetics on top of concentration error doesn’t explain it.
Setting a lower bound on $k_0$ for 2,6-DHAQ

Current Density (mA/cm$^2$)

Potential (V vs SHE)

$E_{0,1} = -0.657$ vs SHE

$k_{0,1} = 7 \times 10^{-4}$ cm/s

$E_{0,2} = -0.717$ vs SHE

$k_{0,2} = 7 \times 10^{-4}$ cm/s
Sequential 1 e⁻ transfers could explain CV

- 2,6-DHAQ
- Model \( i_1 \)
- Model \( i_2 \)
- Model \( i_1 + i_2 \)