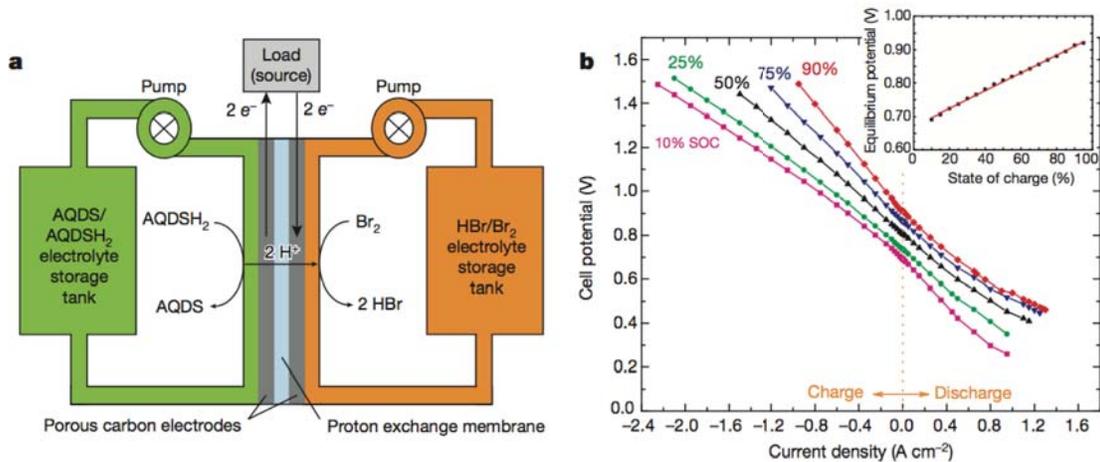


Problem Set 1 – Equivalent Circuit Models



© Macmillan Publishers Limited. Huskinson, B., M. P. Marshak, et al. "A Metal-free Organic-inorganic Aqueous Flow Battery." *Nature* 505 (2014): 195–98. All rights reserved. This content is excluded from our Creative Commons license. For more information, see <http://ocw.mit.edu/help/faq-fair-use/>.

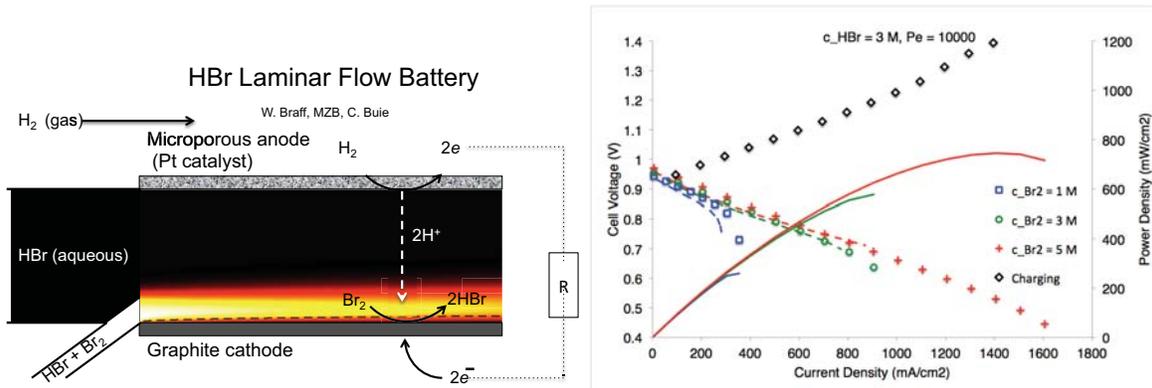


Figure 1: Comparison of two new bromine flow battery technologies. Top: Proton-exchange membrane based **Quinone-Bromine Flow Battery** (QBFB) of Huskinson et al., *Nature* (2014). Bottom: **Membraneless Hydrogen-Bromine Flow Battery** (HBFB) of Braff et al., *Nature Communications* (2013). Left: Cell schematics. Right: Experimental polarization curves.

© Macmillan Publishers Limited. Braff, W. A., M. Z. Bazant, et al. "**Membrane-less Hydrogen Bromine Flow Battery**." *Nature Communications* 4, no. 2346 (2013). All rights reserved. This content is excluded from our Creative Commons license. For more information, see <http://ocw.mit.edu/help/faq-fair-use/>.

1. **Bromine Flow Battery Comparison: Performance** See Figure 1. In the following assume 50% SOC for the QBFB and 3M Br₂ for the HBFB.

- (a) Which cell has the higher open circuit voltage?
- (b) Which cell shows some signs diffusion limitation? Explain your reasoning.
- (c) Estimate the internal resistance R_{int} and of each cell in $\Omega\cdot\text{cm}^2$, and assume R_{int} is constant in the following calculations. Which cell has higher internal resistance, and why?
- (d) Calculate the maximum power density P_{max} (W/cm^2) and the corresponding current density I_{max} (A/cm^2) of each cell on discharge. Which cell has greater power?
- (e) Calculate the voltage efficiency of charge/discharge cycles at 25% and 100% of $\pm I_{max}$ for each cell. Which cell is more efficient?

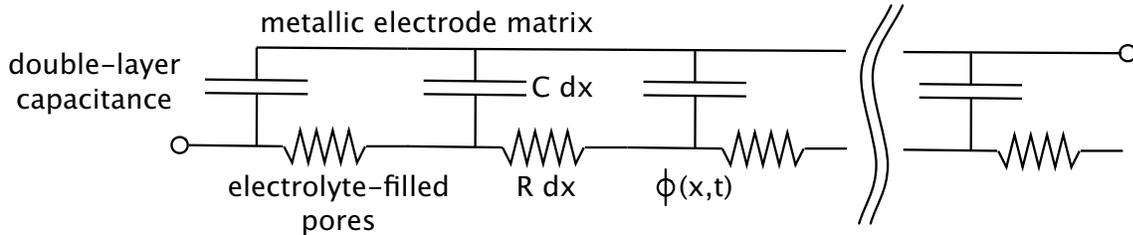
2. **Bromine Flow Battery Comparison: Cost** See Figure 1. In the following assume 50% SOC and 1M quinone for the QBFB and 3M Br₂ for the HBFB.

- (a) Estimate the *power cost* ($\$/\text{kW}$) for each cell discharging at $0.2 \text{ W}/\text{cm}^2$. Assume hardware costs of $\$0.003/\text{cm}^2$ per active area for both cells. The Nafion 212 membrane in the QBFB costs $\$0.26/\text{cm}^2$, while no membrane is needed for the HBFB. The anode catalyst in the HBFB (platinum) costs $\$0.01/\text{cm}^2$, while no anode catalyst is needed for QBFB. Neither cell needs any catalyst for bromine reduction at the cathode. Which cell is cheaper per power? Can either one beat lead-acid and Li-ion batteries ($\approx \$200/\text{kW}$)?
- (b) Estimate the *capacity cost* or energy cost ($\$/\text{kWh}$) for each cell, assuming slow cycling near the open circuit voltage. In flow batteries, the capacity cost is dominated by that of the active materials stored in large separate tanks and the cost of the tanks themselves. The quinones cost $\$4.74/\text{kg}$ with molecular mass 100 g/mol per electron transferred (where 2 electrons are transferred per mole of quinone). Hydrogen (H₂) costs $\$120/\text{kg}$ and has mass 1 g/mol per electron transferred. Bromine (Br₂) costs $\$1.76/\text{kg}$ and has mass 80 g/mol per electron transferred. The cost to store H₂ in tanks at 10,000 PSI is $\$500/\text{kg}$, cost to store the bromine and quinone is $\$1.5/\text{L}$. The cost to operate a liquid pump for bromine or quinone is $\$0.03/(\text{L}\cdot\text{min})$, and pumps are operated for 1 hour per cycle. Which cell is cheaper per energy stored? Can either one beat the lead-acid battery ($\approx \$200/\text{kWh}$) or the Li-ion battery ($\approx \$400/\text{kWh}$)? Can either cell beat the cost target $\$100/\text{kWh}$ to make solar or wind energy more competitive?

3. **Battery discharge at constant load.** Consider a battery whose open-circuit voltage varies with charge $Q(t)$ stored in the cathode as $V_O(Q) = V^0(1 - \alpha Q - \beta Q^2)$, where $\alpha, \beta > 0$. Consider slow discharge against an external resistance R from $Q(0) = 0$, and neglect any internal resistance.

- (a) What is the maximum capacity $Q_{max}(\alpha, \beta)$ for galvanic discharge?
- (b) Solve for the voltage profile, $V(t)$ if $\beta = 0$.
- (c) Solve for $V(t)$ with $\alpha, \beta > 0$.

4. **Super-capacitor polarization.** As shown in the figure, a super-capacitor, consisting of two parallel-plate porous metal electrodes soaked in an electrolyte, can be modeled by a transmission-line equivalent circuit. Assume a symmetric situation of two identical porous electrodes of thickness L , and thus focus on only one, in the region $0 < x < L$. The electrolyte-filled pore space has a constant volume-averaged resistance per length R and constant capacitance per unit length C . Neglect any resistance in the porous metal electrode or the thin gap between the electrodes.



- (a) Show that the mean potential in the pores satisfies a linear diffusion equation

$$RC \frac{\partial \phi}{\partial t} = \frac{\partial^2 \phi}{\partial x^2}$$

with boundary conditions $\phi(0, t) = V(t)$, $\frac{\partial \phi}{\partial x}(0, t) = I(t)R$, and $\frac{\partial \phi}{\partial x}(L, t) = 0$, where $V(t)$ is (half of) the voltage across the electrodes.

- (b) Suppose the supercapacitor begins fully charged at voltage V and for $t > 0$, the voltage is suddenly removed, $V = 0$ (short circuit). Find a separable solution, $\phi_{sep}(x, t) = \Phi(t)\theta(x)$ up to a multiplicative constant, which is valid at long times. What is the time scale for discharging? Estimate the constant by requiring $\frac{1}{L} \int_0^L \phi_{sep}(x, 0) dx = V$.

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