Supplementary Information

Lifetime and Cost of Redox-Active Organics for Aqueous Flow Batteries

Fikile R. Brushett [§,*], *Michael J. Aziz* [†,*], *and Kara E. Rodby* [§]

§ Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
† John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA
*brushett@mit.edu (Fikile R. Brushett); maziz@harvard.edu (Michael J. Aziz).

Techno-economic Calculations

Capital cost (C_{capital}) is calculated by summing the electrolyte cost ($C_{\text{electrolyte}}$) the net present value of the future costs of electrolyte replacement ($NPV(C_{\text{electrolyte}})$), and the power costs ($C_{\text{power}}$) divided by the duration (d):

$$C_{\text{capital}}\ (\$/\text{kWh}) = C_{\text{electrolyte}} + \frac{C_{\text{power}}}{d} + NPV(C_{\text{electrolyte}}) \qquad \textbf{(S1)}$$

$C_{\text{electrolyte}}$ is calculated using a bottom-up approach developed by Dmello *et al.* [1]:

$$C_{\text{electrolyte}}\ (\$/\text{kWh}) = \frac{\left[\dfrac{c^{+}_{\text{active}} \bullet s^{+} \bullet MW^{+}}{\chi^{+} \bullet n^{+}_{\text{e}}} + \dfrac{c^{-}_{\text{active}} \bullet s^{-} \bullet MW^{-}}{\chi^{-} \bullet n^{-}_{\text{e}}} + 2 \bullet r_{\text{avg}} \bullet MW_{\text{salt}} \bullet c_{\text{salt}} + \dfrac{2}{b_{\text{avg}}} \bullet c_{\text{solvent}}\right]}{F \bullet U \bullet \varepsilon_{\text{sys,d}} \bullet \varepsilon_{\text{v,d}} \bullet \varepsilon_{\text{q,rt}}} \qquad \textbf{(S2)}$$

where the names of most variables are listed in **Table S1**. r_{avg} is the mean molar salt ratio (mol/mol), MW_{salt} and c_{salt} are the molecular weight (kg/mol) and cost of the supporting salt ($/kg), respectively, b_{avg} is the mean actives molality (mol/kg), and c_{solvent} is the cost of solvent ($/kg). The + and – superscripts denote the positive and negative electrolyte, respectively.

Here, we assume a symmetric electrolyte, meaning the costs and technical properties are the same for the positive and the negative electrolytes (note: this holds for the vanadium redox flow battery). Additionally, we assume that for aqueous systems the costs of the active species are significantly more than those of the solvent and salt ($c_{solvent} + c_{salt} << c_{active}$) [1,2]. With these two assumptions, we reduce Equation S2:

$$C_{electrolyte}\ (\$/\text{kWh}) = \frac{2 \bullet \dfrac{c_{active} \bullet s \bullet MW}{\chi \bullet n_e}}{F \bullet U \bullet \varepsilon_{sys,d} \bullet \varepsilon_{v,d} \bullet \varepsilon_{q,rt}} \qquad \textbf{(S3)}$$

We take the baseline values for the variables in this equation from the Dmello *et al*. paper, as listed in **Table S1** [1].

Table S1 – Variable names, symbols, units, and baseline values for capital calculations (equations S1-S5). Most values are taken from Dmello *et al.* (2016) [1], which followed the work of Darling *et al*. (2014) [2], and correspond to future cost and performance projections. Other parameters were estimated based on the literature and best guesses at future projections.

Variable Name	Symbol	Units	Baseline Value
Open circuit potential	U	V	1
Depth of discharge	χ	-	0.8
Voltage discharge efficiency	$\varepsilon_{v,d}$	%	91.6%
System discharge efficiency	$\varepsilon_{sys,d}$	%	94%
Round-trip coulombic efficiency	$\varepsilon_{q,rt}$	%	97%
Stoichiometric coefficient	s	-	1
Number of electrons per s formula unit	n_e	-	1
Cost of active species	c_{active}	\$/kg	12.5
Molecular weight of active species	MW	g/mol	150
Cost per unit area	c_a	\$/m^2 of active area	122.5
Balance-of-plant costs	c_{BOP}	\$/kW	102.5
Additional costs	c_{add}	\$/kW	87.5
Area-specific resistance	ASR	Ω-cm^2	1
Discount rate	r	-	0.08
Operational lifetime	n	years	20
Annual electrolyte replacement fraction	f	-	0.15

C_{power} is calculated using a similar bottom-up approach from Dmello *et al.* [1]:

$$C_{\text{power}}\ (\$/\text{kW}) = \frac{c_{\text{a}} \bullet ASR}{\varepsilon_{\text{sys,d}} \bullet \varepsilon_{\text{v,d}} \bullet (1-\varepsilon_{\text{v,d}}) \bullet U^2} + c_{\text{BOP}} + c_{\text{add}} \qquad \textbf{(S4)}$$

where the names of most variables are listed in **Table S1**.

Finally, the net present value of the future costs of electrolyte replacement is calculated using a classic net present value equation:

$$NPV(C_{\text{electrolyte}}) = C_{\text{electrolyte}} \bullet f \bullet \sum_{t=1}^{n\text{-}1} \frac{1}{(1+r)^t} = C_{\text{electrolyte}} \bullet f \bullet \frac{(1+r)^{-1} - (1+r)^{-n}}{1-(1+r)^{-1}} \qquad \textbf{(S5)}$$

where the definition of $C_{\text{electrolyte}}$ can be found in equations S2 and S3. All analyses in **Figure 5** of the main text use the baseline values in **Table S1** unless specified otherwise.

In **Figure 5**, we further define a new variable called the "total active cost," ($C_{\text{active}}^{\text{total}}$):

$$C_{\text{active}}^{\text{total}} = c_{\text{active}} \bullet \left[1 + f \bullet \frac{(1+r)^{-1} - (1+r)^{-n}}{1-(1+r)^{-1}}\right] \qquad \textbf{(S6)}$$

This variable encompasses all of the effects of the cost of active species and its periodic replacement. We can further encapsulate the other important, tunable parameters of organics (i.e., molecular weight and number of electron transfers per mole of active species) that will strongly affect the electrolyte and thus capital costs by transforming the active cost from a weight basis to a charge basis:

$$c_{\text{active}}\ (\$/\text{kAh}) = \frac{c_{\text{active}}\ (\$/\text{kg}) \bullet MW}{F \bullet n_{\text{e}}} \bullet 3.6\text{ e}6\ (\text{C/kAh}) \qquad \textbf{(S7)}$$

Finally, there is a comparison to the capital cost of an all vanadium redox flow battery (VRFB) in **Figure 5a** of the main text. All baseline values for the parameters in **Table S1** were used, except for the open circuit voltage (changed to 1.4 V), the electrolyte replacement fraction (changed to 0, as rebalancing for VRFBs allows essentially infinite electrolyte lifetime), and the active cost on a per charge basis. To calculate the active cost, which corresponds to the green line in **Figure 5a** of the main text, is the average price for Chinese vanadium pentoxide flake (98% purity by weight), calculated from daily price data from the past three years [3]. Daily prices were linearly interpolated in the limited regions where data points were not provided. The shaded green regions represent the +/- standard deviation from the mean (n = 1,093). Values for vanadium pentoxide prices were converted from units of $/kg into $/kAh using the following equation:

$$c_{\mathrm{V}}\ (\$/\mathrm{kAh}) = \frac{c_{\mathrm{V_2O_5}}\ (\$/\mathrm{kg}) \bullet MW_{\mathrm{V_2O_5}}\ (\$/\mathrm{kg\ V_2O_5}) \bullet 3.6\ \mathrm{e}6\ (\mathrm{C/kAh})}{w_{\mathrm{V_2O_5}} \bullet F\ (\mathrm{C/mol\ e^-}) \bullet 2\ (\mathrm{mol\ e^-\ /\ mol\ V_2O_5})} \qquad \textbf{(S8)}$$

where c_V is the price per kAh of vanadium, $C_{V_2O_5}$ is the price per kg of vanadium pentoxide (27.22 +/- 14.90 $/kg), $MW_{V_2O_5}$ is the molecular weight of vanadium pentoxide (181.88 e-3 kg/mol), and $w_{V_2O_5}$ is the weight purity of vanadium pentoxide (0.98).

References

[1] R. Dmello, J.D. Milshtein, F.R. Brushett, K.C. Smith, Cost-driven materials selection criteria for redox fl ow battery electrolytes, J. Power Sources. 330 (2016) 261–272. doi:10.1016/j.jpowsour.2016.08.129.

[2] R.M. Darling, K.G. Gallagher, J.A. Kowalski, H. Seungbum, F.R. Brushett, Pathways to low-cost electrochemical energy storage : a comparison of aqueous and nonaqueous flow batteries, (2015) 3459–3477. doi:10.1039/C4EE02158D.

[3] Vanadium Price, (2019). https://www.vanadiumprice.com/ (accessed December 18, 2019).