Lab exercise 3:

An Organic Redox (Flow) Battery

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1 Introduction

In order for the electricity generation transition to move away from fossil fuels and towards renewable energy sources, energy storage technologies must be implemented. Redox flow batteries are a promising candidate for this purpose. Organic redox flow batteries are of great interest since they do not require rare earth elements and are thus not dependent on mining activity and location specific materials. Redox flow batteries promise impressive scaling of energy storage costs and allow for decoupling of storage capacity and power. The aim of this report is to investigate the properties of a static organic redox (flow) battery. The properties studied include: redox potential, cell voltage, capacity, efficiency, state of charge, and volumetric energy density. Finally, the report touch upon the amount of Alizarin Red S (ARS) negolyte required to store the amount of energy that corresponds to the average power consumption of a typical household.

2 Methodology

The experiments used the organic compound ARS as the negolyte and Ferrocyanide as the posolyte. ARS is a redox active compound which reacts with a two-electron response. The experiment started off with the Ferrocyanide in its reduced form and ARS in its oxidized form.

2.1 Cyclic Voltammetry

The redox potential of the posolyte and negolyte were investigated utilizing cyclic voltammetry with a scanrate of 50 mV/s. The CV data were recorded in a three-electrode setup with a supporting electrolyte 1 M KOH and either 2 mM ARS or 2 mM Ferrocyanide as the redox active compound.

2.2 Organic Redox (Flow) Battery

An open (flow) cell battery was assembled in accordance with instructions, consisting of an ion-exchange membrane, Viton gaskets, porous carbon felt electrodes, and a plastic cell with four glassy carbon rods inserted. The two compartments were filled with 1.8 mL of posolyte at a concentration of 0.2 M on one side and 2.3 mL of negolyte at a concentration of 0.05 M on the opposing site. The cell used porous carbon felt electrodes with a geometric area of 5 cm^2.

2.2.1 Charge-discharge experiment

The theoretical capacity of the posolyte and negolyte were calculated with Faraday's Law, using the provided concentration of active material and absorbed electrolyte volume. Faraday's law is displayed in equation 1.

$$Q = nCVF \tag{1}$$

The current needed to discharge or charge the cell in 20 minutes was calculated. The battery was then cycled through three charge-discharge cycles with cutoff voltages of 0.6 V for the discharge and 1.5 V for the charge, the collected data were used to determine coulombic, voltage, and electrical efficiency according to equation 2, 3, and 4.

$$\epsilon_{columbic} = \frac{Q_{discharge}}{Q_{charge}} \tag{2}$$

$$\epsilon_{voltage} = \frac{\overline{E}_{cell,discharge}}{\overline{E}_{cell,charge}} \tag{3}$$

$$\epsilon_{electrical} = \epsilon_{voltage} \cdot \epsilon_{coulombic} \tag{4}$$

2.2.2 State of charge

The complete cell potential as function of the state of charge (SOC) were investigated using the experimental peak potentials from the CV and a simplified expression on a Nernstian form. In order to look into the relation between the complete cell potential and the SOC, the redox potentials of the redox couple must be determined. The redox potential, $E^{0'}$ of the posolyte and negolyte, was assumed to be equal to the half-cell potential, $E_{1/2}$, when the diffusion coefficients of oxidized and reduced species are equal. Since the flow cell is considered capacity-balanced this assumption is applicable and the redox potentials can thus be calculated using equation 5, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials from the CV.

$$E^{0'} \approx E_{1/2} = \frac{E_{pa} + E_{pc}}{2} \tag{5}$$

The redox potential of both the posolyte, $E^{0'}_{pos}$, and the negolyte, $E^{0'}_{neg}$, were calculated. The complete cell potential can then be expressed with equation 6 below. Where $p = n^0_{Ferro}/2n^0_{ARS}$, $p = n^0_{Ferri}/2n^0_{ARS}$, and n^0_{Ferro}, n^0_{Ferri}, n^0_{ARS} are the initial molarities of ferrocyanide, ferricyanide, and total molarity of ARS (reduced and oxidized).

$$E^{0'}_{cell} = E^{0'}_{pos} - E^{0'}_{neg} + \frac{RT}{2F} \cdot ln\left(\frac{SOC}{1-SOC} \cdot \left(\frac{q+SOC}{p-SOC}\right)^2\right) \tag{6}$$

2.3 Volumetric capacity and energy density

The volumetric capacity of the flow cell were calculated with equation 7, where U is the cell voltage and n_{tanks} is the number of tanks. The number of tanks being two in our case.

$$Q_{volumetric} = nCF \tag{7}$$

The volumetric energy density (ED) of the flow cell were calculated with equation 8, where U is the cell voltage, and $V_{posolyte}$ is the volume of posolyte corresponding to the capacity of the negolyte, at the given concentrations. This equation was used since the flow cell did not feature the same effective concentration on both sides of the membrane. For a situation with the same effective concentration on both sides equation 9 can be utilised here n_{tanks} is the number of tanks.

$$ED = \frac{nCFUV_{negolyte}}{V_{posolyte} + V_{negolyte}} \tag{8}$$

$$ED = \frac{nCFU}{n_{tanks}} \tag{9}$$

3 Results

All graphs recorded during the experiment, as well as calculations and plots from experimental data are presented in the following section.

3.1 Volumetric capacity

The volumetric capacity (Ah/L) of the electrolytes in the static flow battery cell were calculated with a modified Faraday's law, see equation 1.

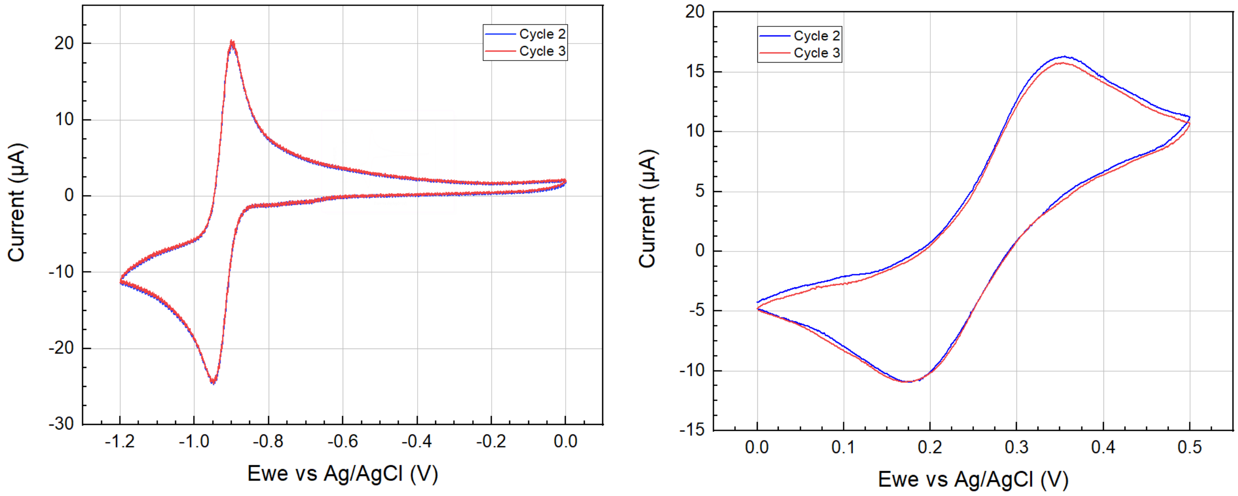
$$Q_{ARS} = \frac{2 \cdot 0.05 \text{ M} \cdot 96485.33 \frac{C}{mol}}{3600 \frac{C}{Ah}} = 2.68014811 \text{ Ah/L} \tag{10}$$

$$Q_{Ferrocyanide} = \frac{1 \cdot 0.2 \text{ M} \cdot 96485.33 \frac{C}{mol}}{3600 \frac{C}{Ah}} = 5.360296 \text{ Ah/L} \tag{11}$$

Thus, ARS and Ferrocyanide have a volumetric capacity of 2.68 Ah/L and 5.36 Ah/L respectively.

3.2 Cyclic Voltammetry

The CV of ARS and Ferrocyanide resulted in the graphs presented in figure 1.



(a) ARS

(b) Ferrocyanide

Figure 1: Cyclic Voltammetry of ARS and Ferrocyanide in 1 M KOH at 50 mV/s.

From the CV, the peak potentials of both compounds were located and the values are presented in table 1.

Table 1: Peak potentials of the posolyte and negolyte based on cyclic voltammetry peak readings.

	E_{pa}	E_{pc}
ARS	-0.9	-0.94
Ferrocyanide	0.35	0.17

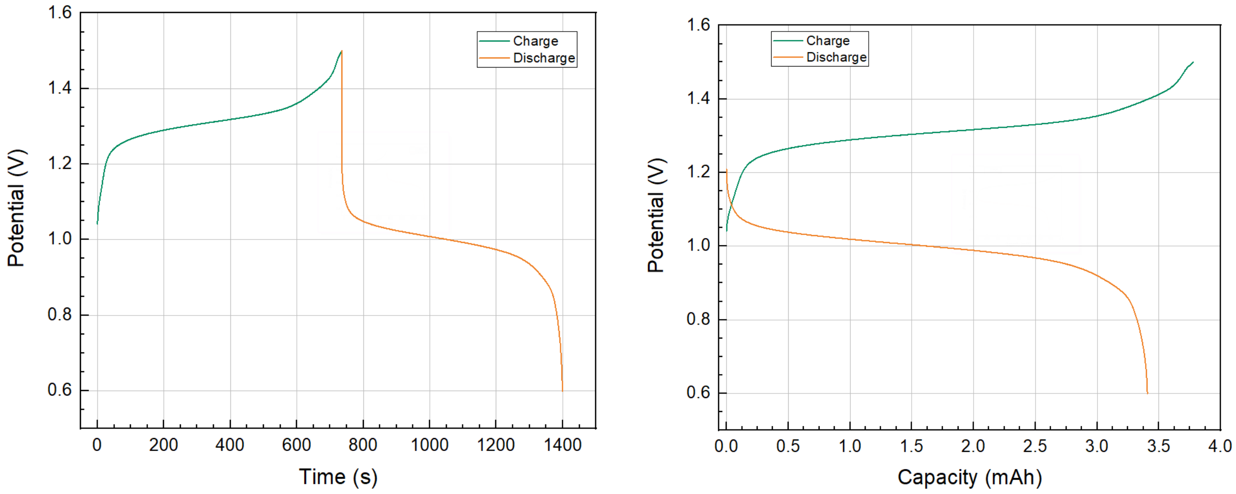
3.3 Charge-discharge experiment

The theoretical capacity of the posolyte and negolyte was:

$$Q_{posolyte} = 1 \cdot 0.2 \text{ mol/L} \cdot 1.8 \text{ mL} \cdot 26.8015 \text{ Ah/mol} = 9.6485 \text{ mAh} \tag{12}$$

$$Q_{negolyte} = 2 \cdot 0.05 \text{ mol/L} \cdot 2.3 \text{ mL} \cdot 26.8015 \text{ Ah/mol} = 6.164 \text{ mAh} \tag{13}$$

The charge-discharge experiment resulted in the two graphs displayed in figure 2 below. The full cycle took 23.3 minutes to complete and were charged/discharged with 18.5 mA for at C-rate of 3C based on the limiting capacity.



(a) The cell voltage (V) vs time (s)

(b) The cell voltage (V) vs capacity (mAh)

Figure 2: Charge-discharge experiment

The coulombic efficency is equal to the ratio between the extracted capacity during discharge and charge. In accordance with equation 2 it was calculated to be 91.9%.

$$\epsilon_{coulombic} = \frac{3.4 \text{ mAh}}{3.7 \text{ mAh}} \approx 91.9\% \tag{14}$$

According to equation 3 the voltage efficiency is equal to the ratio of the average voltages of the cell when discharging and charging. The resulting voltage efficiency is about 80,3%.

$$\epsilon_{voltage} = \frac{1.024 \text{ V}}{1.276 \text{ V}} \approx 80.3\% \tag{15}$$

The electrical efficiency equals the product between voltage efficiency and coulombic efficiency, this gives us:

$$\epsilon_{electrical} = 0.803 \cdot 0.919 = 73.8\% \tag{16}$$

3.4 State of charge

The half-wave redox potentials were calculated using equation 5, resulting in a potential of 0.26 V for Ferrocyanide and -0.92 V for ARS. After that the overall cell potential was calculated using the Nernst equation and the initial concentrations of oxidised and reduced species, C_O and C_R as 0.2 M and 0.05 M.

$$E = E_i^0 + \frac{RT}{nF} ln \frac{C_O}{C_R} = 0.26 + 0.92 + \frac{8.3145 \cdot 298.15}{2 \cdot 96485} \cdot \frac{0.2}{0.05} = 1.23V \tag{17}$$

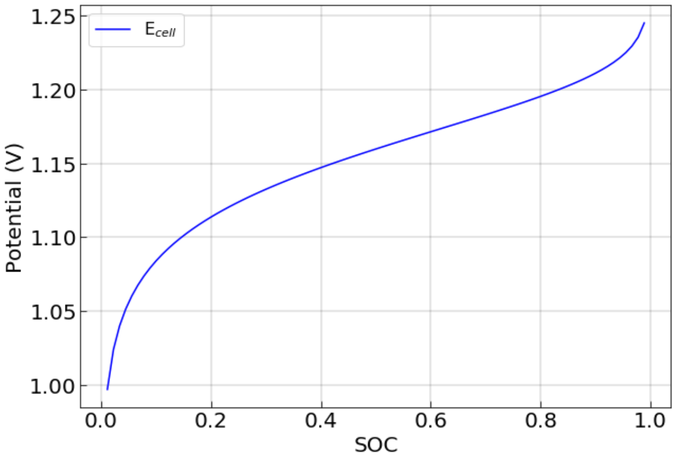


Figure 3: The predicted cell potential (E$_{cell}$) as a function of SOC.

3.5 Volumetric energy density

The volumetric energy density of the investigated flow battery were calculated to be 2.1977 Wh/L using equation 8. The calculation is presented below in equation 18.

$$ED_{0.05M} = \frac{2 \cdot 0.05 \text{ mol/L} \cdot 26.8015 \text{ Ah/mol} \cdot 1.23\text{V} \cdot 2.3\text{mL}}{2.3 \text{ mL} + 1.15 \text{ mL}} \approx 2.1977 \text{ Wh/L} \tag{18}$$

The given maximum solubility of ARS in 1 M KOH is 0.55 M, assuming the cell potential is the same as the one calculated for the ARS-Ferrocyanide flow battery we can then calculate the achievable volumetric energy density assuming the posolyte capacity is matched and have the same effective concentration as the negolyte using equation 9 and setting the number of tanks to 2.

$$ED_{0.55M} = \frac{2 \cdot 0.55 \text{ mol/L} \cdot 26.8015 \text{ Ah/mol} \cdot 1.23 \text{ V}}{2} \approx 18.15 \text{ Wh/L} \tag{19}$$

4 Discussion

From the volumetric capacity calculations and the fact that 1.8 mL of posolyte and 2.3 mL of negolyte was used in the testing we see the flow cell did not have the same effective concentration of electrolytes. Therefore we calculated the volumetric energy density utilising a posolyte volume corresponding to a capacity balanced cell. An argument can be made for including the total volume of posolyte in the calculation and not just the volume corresponding to a capacity balanced cell as this would reflect the entirety of electrolyte used. When looking at the achievable volumetric energy density it appears quite promising for an organic compound, when state of the art vanadium cells have a volumetric energy density of 33 Wh/L. If considering a household with an energy demand of 20kWh a flow cell with ARS negolyte at a concentration 0.55 M would need 1103 L of ARS negolyte to meet the energy demand, assuming an identical cell potential to the one found in the experiments.

$$V_{negolyte} = \frac{20 \text{ kWh}}{18.13 \text{ Wh/L}} \approx 1103 \text{ L} \tag{20}$$

In the charge-discharge experiment we only extracted around 3.4 mAh compared to the theoretical of 6.164 mAh. The extracted capacity can be lower for multiple reasons such as, bubble formation, poor surface contact, the fast charge/discharge current, or diffusion layer depletion. many of these possible contributors to capacity loss can be attributed to the simple open (flow) cell constructed. In a closed state of the art setup, with flow the extracted capacity would likely exceed 55% on a discharge.

Redox flow batteries have been proposed as an option for electricity grid balancing and support. A discharge time of multiple hours would have an effect on the voltage and electrical efficiency of the cell. In the performed experiment the cell was charged/discharged with a current corresponding to 3C (20 minutes) and as such we are trying to draw current much faster compared to a charge/discharge time of 5 hours (C/5). For the 3C experiment the overpotential will be larger than for the C/5 charge/discharge. We therefore expect the average voltage under charging to be closer (lower) to the equilibrium cell potential and the average voltage under discharge to be closer (higher) to the cell potential. The voltage efficiency will increase as the numerator ($E_{discharge}$) will be larger and the denominator (E_{charge}) will decrease, both contributing to a larger voltage efficiency. For the electrical efficiency we expect it to increase due to the increase in voltage efficiency, we would also expect the coulombic efficiency to increase at the lower C-rate as a result of more capacity being extracted since the heat generated and ohmic losses and will be lower at lower currents. This will also increase the electrical efficiency, overall the charging/discharging at longer times will increase the voltage and electrical efficiency.