Optimizing TEMPO Concentrations For Non-Aqueous Redox Flow Batteries

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Introduction

Motivation

While alternative energy sources continue to improve, there remains the problem of storing the excess energy[1]

Redox Flow Batteries

Redox Flow batteries could be the answer to this problem:

- Power decoupling[2]
  - Scalability
  - Flexibility
- Organic non-aqueous redox flow batteries[2]
  - Abundant
  - High tunability
  - Safety

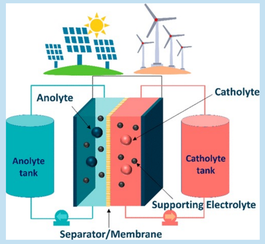

Fig 1. Diagram of a typical RFB[3]

- Electrolyte: Tetrabutylammonium Hexafluorophosphate ($TBAPF_6$)
- Analyte: 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)
- Viscosity

Rotating Disk Electrode (RDE)

- Cyclic Voltammetry (CV)
- At higher concentrations, higher viscosity creates too much resistance for standard CV to provide useful data
- RDE solves this with convection-based mass transport[4]

Objective

- Optimize concentration for Redox Flow Batteries
  - Test different concentrations of TEMPO and $TBAPF_6$
  - Calculate Diffusion coefficient and electron transfer constant

Methodology

Solution Preparation

1. Desired amount of TEMPO and $TBAPF_6$ were massed into a volumetric flask and acetonitrile was poured to the 50mL mark
2. Density was calculated by massing the flask before and after and the solution was transferred to a 3-neck round bottom flask

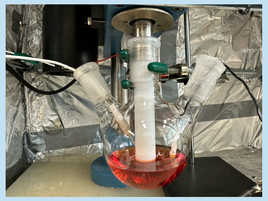

Fig 2. Solution in round bottom flask with electrodes

Fig 3. Mechanically polishing working electrode

Polishing Electrodes

3. The 5 mm platinum disk working electrode was mechanically polished in aqueous slurries of 3.0μm, 1μm, and 0.5μm alumina powder, rinsing between each grit
4. A hydrogen flame was used to flame polish the platinum coil counter electrode
5. For reference electrode, a non-aqueous Ag/Ag+ reference electrode was used

Setup

7. Working electrode was attached to Pine AFASR Analytical Rotator inside Faraday cage
8. The round bottom was clamped under working electrode and the three electrodes were placed in the solution while being connected to the CHI1100B potentiostat

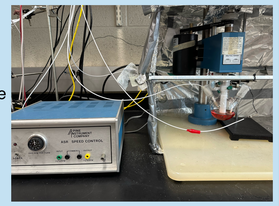

Fig 4. Full Apparatus

Measurements

9. Cyclic Voltammetry scans were run at six different rotation speed at a scan rate of 10 mV/s
10. Viscosity of solution was taken using a plate DV2T-LV viscometer with CPA-40Z and Brookfield cone equipped with a TC-550 temperature control at 25°C

Results

TEMPO:$TBAPF_6$ (mM)	ρ (g/mL)	μ (cP)	ν (cm^2/s)
10:100	0.780	0.390	0.00500
10:200	0.810	0.440	0.00543
100:500	0.843	0.575	0.00682
200:500	0.847	0.567	0.00669
250:1250	0.941	0.917	0.00974

Table 1. The density (ρ) and dynamic viscosity (μ) was recorded for each of the five concentrations. The kinematic viscosity (ν) was then calculated by dividing μ by ρ

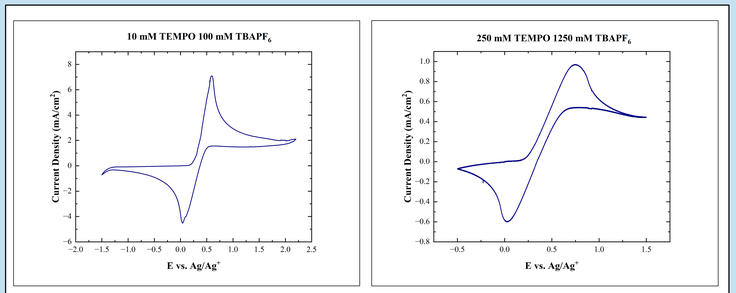

Fig 5. Cyclic voltammograms ran at 0 RPM for the lowest (left) and highest (right) concentrations

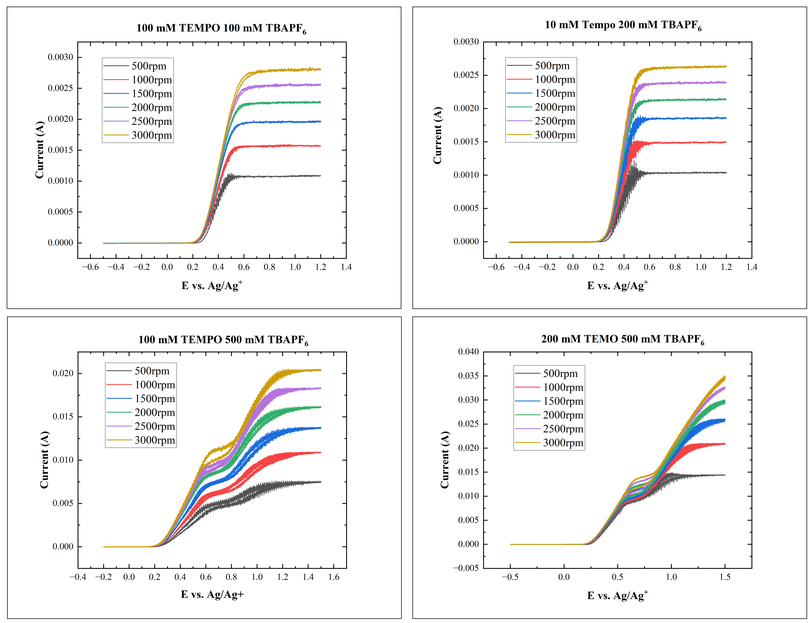

Fig 6. Voltammograms were taken at rotation speeds of 500, 1000, 1500, 2000, 2500, and 3000 RPM for each of the five concentrations. The potential applied on the top two ranged from -0.5V to 1.2V while it ranged from -0.5V to 1.5V for the three on the bottom. Note that the bottom three have two plateau each but the ones of interest take place around 0.6-0.8V.

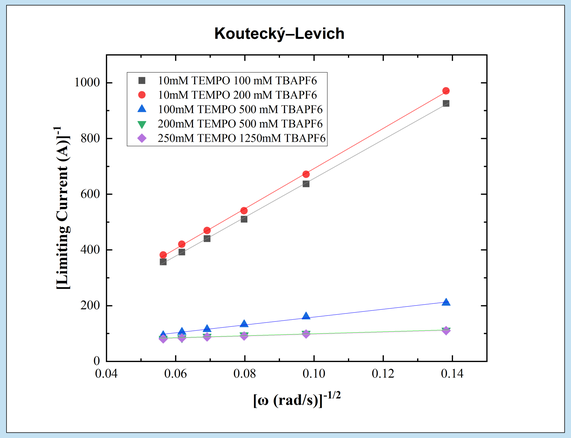

Fig 7. The Koutecký-Levich graph was created by plotting the inverse square root of the rotation speed by the inverse of the limiting current, which can be found from the peaks in Fig 5. Note that the purple and green lines overlap each other due to having very similar equations.

TEMPO:$TBAPF_6$ (mM)	D (cm^2/s)	K^0 (cm/s)
10:100	0.00001870	0.1310
10:200	0.00001910	0.1880
100:500	0.00000330	0.0300
200:500	0.00000041	0.0042
250:1250	0.00000033	0.0034

Table 2. The diffusion coefficient (D) was calculated using the Levich equation and the heterogenous electron transfer rate constant was calculated from the Butler-Volmer equation.

Discussion

- Take average of all values in the plateau to get limiting current
- Plug all known values into the Levich equation to calculate diffusion coefficient (D)[4]

$$I_L = 0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C$$

- Where I_L is the limiting current, n is the number of electrons transferred, F is Faraday's constant, A is the area of the working electrode surface, ω is the rotation rate, ν is the kinematic viscosity, and C is the concentration of analyte
- Simplification of Butler-Volmer's equation can be derived to calculate heterogenous electron transfer rate constant[5]

$$I_k = nFAk^0C$$

- Where I_k is the kinetic current, which is found by taking the inverse of the intercept from the Koutecký-Levich graph

Conclusion

- Lower concentration of TEMPO produced expected sigmoidal curve
- Higher concentrations had two plateaus instead of one
- 10 mM TEMPO and 200 mM $TBAPF_6$ appears to be the most effective
- No definitive trend between viscosity and D or K^0
- Higher ratio of $TBAPF_6$ to TEMPO tended to yield a greater D and K^0

Next Steps

- Investigate higher concentrations
  - Smaller electrode surface area
  - Higher RPM
  - Determine the cause of the 2nd plateau on higher concentrations

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