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Voltammetry study of quinoxaline in aqueous electrolytes

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ABSTRACT

Organic compounds have recently received considerable attention as active materials in redox flow batteries (RFBs) due to their good electrochemical reversibility, high theoretical energy densities, and promise for low cost production. Until now, organic active material candidates for aqueous RFBs have been limited to the quinone family, a set of aromatic-derived organic molecules, distinguished by an even number of ketone (R—C(=O)—R′) groups. This work aims to elucidate and optimize the electrochemical behavior of quinoxaline, an organic molecule consisting of fused benzene and pyrazine rings, in aqueous electrolytes. More than 30 electrolytes are screened by cyclic voltammetry, and the five most promising electrolytes are investigated further using rotating disk voltammetry. Electrochemical behavior of quinoxaline shows pH dependent thermodynamics and reaction mechanisms, while chloride-containing supporting electrolytes greatly enhance solubility. This study sheds light on the promising characteristics of quinoxaline as a low potential compound for aqueous RFBs; quinoxaline has a redox potential of $E^\circ \approx -0.02$ V vs. RHE, is soluble up to ~4.5 M in water, exhibits a two-electron transfer capability, and possesses a low molecular weight (130.15 g mol^{-1}), resulting in a theoretical capacity of 410 mAh g^{-1}.

1. Introduction

Aqueous redox flow batteries (RFBs) utilizing organic redox active materials have recently received considerable attention due to a number of promising attributes when compared to aqueous RFBs employing inorganic active materials. Transition metal (i.e., all-vanadium) and inorganic non-metallic (i.e., polysulfide-bromine) aqueous chemistries have traditionally been at the forefront of flow battery research due to their reversible redox behavior and high solubility [1,2]. Broad market penetration of aqueous flow battery chemistries founded on the reduction and oxidation of transition metals, however, is limited by the cost and abundance of the redox active species [3]. Further, many inorganic non-metallic aqueous flow batteries (such as those involving bromine) have failed to reach widespread adoption due to their inherently toxic and corrosive nature, making the practical design of pumps, flow fields, storage tanks, and pipes difficult [4]. With the current system costs in the range of \$200–\$600 kWh^{-1}, inorganic aqueous flow batteries are challenged to meet the new target for redox flow batteries of \$100 kW h^{-1} set forth by the United States Department of Energy [3–8]. Organic redox active species offer a new pathway to potentially meeting this target since organic compounds are comprised of earth abundant elements, such as carbon, hydrogen, nitrogen, oxygen, sulfur, etc.; thus, the cost associated with an organic redox active species is not determined by production rates of raw materials or material reserves. Another exciting attribute of organic redox active compounds is their broader design space, which can be accessed via molecular modification. By changing the structure or adding functional groups to organic compounds, many characteristics that are vital to designing a successful RFB system, such as molecular weight, solubility, redox potential, and reversibility, can be rationally controlled.

Electrochemical behavior of redox active organic compounds in aqueous solutions has been studied for nearly a century, with research efforts dating back to the 1920s [9,10]. During this long period, the family of organic compounds termed quinones showed good electrochemical reversibility, leading to further investigation [11–13]. Quinones are a class of aromatic-derived compounds in which an even number of —CH= groups are converted into ketone (R—C(=O)—R') groups, yielding a fully conjugated and cyclic dione structure [14]. Recent research efforts on quinone electrochemistry have focused on identifying compounds with electrochemical characteristics that are well-suited for RFB applications. One such compound is 4,5-dibenzoquinone-1,3-benzedisulfonate (BQBDS), which was proven as a two-electron transfer, high potential redox active material ($E^\circ = 0.72$ V vs. SHE) and demonstrated in a flow cell with a lead (Pb) low potential electrode [15]. Additionally, Huskinson et al. studied the electrochemical behavior of 9,10-

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anthraquinone-2,7-sulfonic acid as a two-electron transfer, low potential redox active material ($E^\circ = 0.23$ V vs. SHE) and demonstrated its cycling performance in a flow cell with the Br_2/Br^- redox couple on the high potential side [16]. Engineering developments coupled BQBDS with anthraquinone-2-sulfonic acid ($E^\circ = 0.09$ V vs. SHE) to create an all-organic aqueous RFB [17]. Beyond quinones, some efforts have also focused on identifying organic redox couple replacements for the I^{3-}/I^- couple, which acts as a mediator in dye sensitized solar cells, in order to minimize the corrosive effects of I^{3-}/I^-. One successful organic redox couple has been the 5-mercapto-1-methyltetrazole ion ($E^\circ = 0.5$ V vs. SHE) [18].

This study aims to explore the electrochemical behavior of quinoxaline as a low potential redox active compound in different aqueous electrolytes, extending the knowledge base of organic redox active compounds beyond the quinone family. The quinoxaline structure is characterized by a benzene ring and a —C—N=C— containing pyrazine ring, as depicted in Fig. 1. A variety of quinoxaline derivatives were studied as component materials in organic sensitizers for dye-sensitized solar cells and as lower band gap materials in organic photovoltaics [19,20]. Triquinoxalinylene specifically was used in a lithium-ion battery application, acting as an organic high potential material [21]. A quinoxaline derivative was also studied as a low potential redox active compound in an all-organic, non-aqueous RFB [22]. Also, a number of studies reported on quinoxaline electrochemistry in non-aqueous solvents [23–27]. Aqueous quinoxaline was recently applied as a redox active compound in a solar-rechargeable RFB device, however, exploration of quinoxaline electrochemical behavior was not the focus of that study [28]. Finally, several studies investigated quinoxaline electrochemical behavior in acidic and near-neutral electrolytes with a focus on determining kinetic rate parameters and related organic chemistry [29–33].

In this work, the electrochemical behavior of quinoxaline was investigated using voltammetric techniques in over 30 aqueous electrolytes, comprised of 12 different supporting salts across the pH range of ca. 4 to 14. Specifically, cyclic and hydrodynamic voltammetry were used to qualitatively and quantitatively assess the electrochemical performance and stability of quinoxaline as a function of supporting salt choice and solution pH. Our studies reveal quinoxaline to be a promising redox active material for aqueous RFBs due to its high solubility in water (~4.5 M) and attractive theoretical energy density of 410 mAh g^{-1}, which is attributed to its low molecular weight (130.15 g mol^{-1}) and ability to store two electrons. The redox potential was found to be $E^\circ \approx -0.02$ V vs. RHE, which is lower than the reported redox potentials of quinones in aqueous solution.

2. Experimental

2.1. Materials

In this work, quinoxaline electrochemical behavior was characterized in a number of aqueous electrolytes, resulting in the use of a large number of chemical compounds. Quinoxaline was purchased from Sigma-Aldrich and had a purity of 99.9%. The suppliers and purities of all salt compounds used are presented in Table 1. Additionally, a table of all electrolyte compositions tested is available in Section 3.1. Deionized water (DI H_2O, 18.2 MΩ) for all solutions was obtained from a Milli-Q system (EMD Millipore). In the specific case of $NaHCO_3$ solution preparation, first a stock Na_2CO_3 solution was prepared, and then gaseous CO_2 was bubbled into the solution for 45 min to create $NaHCO_3$ solution. In all experiments, the quinoxaline concentration was 5 mM, and the supporting salt cation concentration was 1 M.

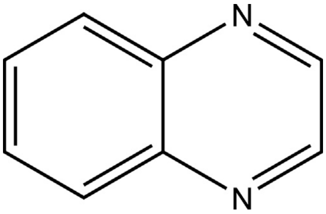

Fig. 1. The molecular structure of quinoxaline.

Table 1
Suppliers and purities of salts used in electrochemical experiments.

Salt	Supplier	Assay (%)	Salt	Supplier	Assay (%)
KCl	Sigma-Aldrich	99.0-100.5	LiOH	Sigma-Aldrich	98
KNO_3	Sigma-Aldrich	99.0	Li_2SO_4	Sigma-Aldrich	99.0
KOH	Sigma-Aldrich	99.99	$NaC_2H_3O_2$	Sigma-Aldrich	99.0
K_2SO_4	Sigma-Aldrich	99.0	Na_2CO_3	Sigma-Aldrich	99.999
LiCl	Fluka	99.0	$NaNO_3$	Sigma-Aldrich	99.0
$LiNO_3$	Sigma-Aldrich	99.99	NaOH	Macron	98.0

2.2. Voltammetry

Cyclic voltammetry (CV) and rotating disk voltammetry (RDV) techniques were employed to probe the electrochemical behavior of quinoxaline. Two separate procedures were used in CV experiments. The first procedure was designed for rapid screening of electrochemical behavior of quinoxaline in many different electrolyte compositions. The second CV procedure was designed for calculating the number of electrons transferred, diffusion coefficients, and transfer coefficients in only the electrolytes with promising electrochemical characteristics. All electrochemical measurements presented in this paper were performed using a Biologic VSP-300 potentiostat. Glassy carbon working electrodes were used in voltammetry experiments and polished with 0.05 μm alumina suspension before performing a new set of measurements. The initial CV scan direction was always cathodic (reductive).

Cell resistances were measured prior to electrochemical experiments to be ~5 Ω. Due to small peak currents during CV (≤1 mA), the maximum estimated iR drop was ~5 mV. During rapid screening CV, an 85% resistance compensation (iR correction) was applied during the experiment to ensure high quality data in untested electrolytes. In promising systems where quantitative CV techniques were applied, no iR correction was initiated as the small potential offset was unlikely to affect experimental results. Additionally, no iR correction was applied during RDV experiments because analyses only considered the limiting RDV current, which is unaffected by ohmic loss. All potentials in this paper are reported versus either the reversible hydrogen electrode (RHE) or the standard hydrogen electrode (SHE). The RHE scale was used to compare voltammetric behavior of quinoxaline over a wide range of pH. The SHE scale was used to evaluate the relationship between solution pH and quinoxaline redox potential. In practice, data was collected using a Ag/AgCl reference electrode, calibrated using methods described in the following sections, and, post-experiment, solution pH was measured using a pH meter (Thermo-Scientific, Orion Star A215). Potentials were then adjusted to the SHE or RHE scale via the Nernst equation. For every CV data set presented in this study, a number of quantitative characteristics were used to determine the electrochemical performance of quinoxaline in a given electrolyte, including redox potential, peak separation, peak currents (anodic and cathodic), and approximate linear slopes before peaks (anodic and cathodic). All experimental