Electrochimica Acta 154 (2015) 462–467

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrochemical characteristics and transport properties of Fe(II)/Fe(III) redox couple in a non-aqueous reline deep eutectic solvent

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ARTICLE INFO

Article history:
Received 26 August 2014
Received in revised form 19 November 2014
Accepted 9 December 2014
Available online 11 December 2014

Keywords:
Iron ions redox couple
Deep eutectic solvent (DES)
Electrochemical characteristics
Transport properties

ABSTRACT

Deep eutectic solvent (DES) is a promising electrolyte for non-aqueous redox flow batteries as it offers unique advantages including a wide electrochemical window, low vapor pressure and ease in preparation. In this work, the electrochemical characteristics of the Fe(II)/Fe(III) redox couple and the transport properties of ferric ions in the reline DES are studied. The cyclic voltammetry (CV) curves show that the redox reaction is quasi-reversible with the charge transfer coefficient of 0.44 at room temperature. The diffusivity, viscosity, conductivity of ferric ions in the reline DES are measured at different temperatures. The results indicate that the transport properties are similar to those for conventional ionic liquids. The high solubility of ferric ions in the reline DES is attributed to the formation of hydrogen bond donors, which is confirmed by the FT-IR absorption spectra analysis.

1. Introduction

Redox flow batteries (RFBs) are promising energy storage systems due to their unique advantages, namely independence of power and energy capacity, long life-span and versatility [1–7]. Existing commercial RFB systems are typically based on the redox couple salts dissolved in aqueous electrolytes. The literature describes aqueous RFBs such as all-vanadium, bromine-polysulfide, iron-chromium and zinc-cerium [8]. Aside from all-vanadium RFBs, all of the aforementioned systems suffer from cross-contamination due to membrane permeability, which leads to electrolyte degradation and capacity loss. Another drawback of the aqueous systems is that the cell voltage is limited by the water electrolysis potential. Finally, the poor thermal stability of conventional RFBs dictates a narrow operating temperature range [6,8].

Non-aqueous systems are able to mitigate these problems due to their unique physical and chemical properties [9]. For instance, some ionic liquids (ILs) have been exploited as non-aqueous electrolytes in RFBs [10–12], which offer significant advantages. Firstly, they can be engineered to be electrochemically stable, allowing high cell voltage. Secondly, due to lower ion diffusivities in ILs, cross-contamination is less of a problem. Lastly, high solubility can be achieved as an electroactive species may be part of the ionic liquid. For example, ILs based on transition-metal ethanolamine cation complexes and discrete organic anions can have electroactive specie concentrations of up to 6.5 M [13].

There are several major challenges for developing the IL-based RFBs that must be addressed before commercialization. High costs and limited availability are the biggest hurdles to overcome. In addition, the preparation of a transition-metal-salt solution requires a complicated metathesis of the desired metal salt from protonated anion [14,15]. To address these issues, the deep eutectic solvents (DESs) are proposed to be the substitutes of ILs. DESs are formed when an organic halide salt is combined with a material capable of forming a complex with the halide, to produce a material that is liquid at ambient condition [16]. The most commonly used DESs are composed of choline chloride (as the halide salt) and different complexing agents, e.g. urea (this DES is named reline), amides, malonic acid, ethylene glycol (this DES is named ethaline) [17]. DESs exhibit similar properties to the chloride-rich ionic liquids, but with a simpler preparation. They are usually non-toxic, biodegradable and tend to be one order of magnitude cheaper than ionic liquids [16,18].

Previous works have been performed on the DESs. Abbott et al. reported the electrochemical properties of copper complexes in a DES for the first time [19]. Lloyd et al. developed an all copper hybrid redox flow battery using the ethaline DES [20]. Both works show that the copper redox flow battery with DES can cycle well with high efficiencies. Due to the exceptional abundance of iron, the Fe(II)/Fe(III) redox couple has also been studied recently. Lloyd et al. developed a Zn-Fe redox flow battery in ethaline DES [21]. The

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http://dx.doi.org/10.1016/j.electacta.2014.12.061
0013-4686/

$[FeCl_4]^-$ complex was found to exist in the DES electrolyte when $FeCl_3$ was used. An energy efficiency of 78% was achieved at a current density of 0.5 mA/cm^2.

Among the DESs, reline has been applied to different electrochemical systems operating at room temperatures, primarily because at room temperatures reline is in liquid form [22] and the decomposition of urea in reline is unlikely [21]. However, the electrochemical characteristics and transport properties of Fe(II)/Fe(III) redox couple in the reline DES have yet to be reported. This paper investigates the electrochemical kinetics of Fe(II)/Fe(III) redox reactions and the solubility of ferric ions in the reline DES, together with the viscosity and conductivity of the DES within a wide temperature range. The results show that the redox reaction is quasi-reversible with a charge transfer coefficient of 0.44, and the transport properties of ferric ions in reline DES are comparable to that in the conventional ionic liquids.

2. Experimental

2.1. Preparation of electrolyte

The reline DES electrolyte was prepared by combining choline chloride (Sigma-Aldrich 99%) and urea (Sigma-Aldrich 99.5%) using a 1:2 molar ratio. The solution was heated and stirred at 100 °C until a liquid was formed, at which point the temperature was reduced to the room temperature. At room temperature the density of the reline DES is measured to be 1.05 kg/L. The electrolyte used in all experiments was prepared by adding anhydrous $FeCl_3$ (Fluka 97%) to DES to form a 1.0 M non-aqueous.

2.2. Electrochemical characterizations

The CV tests were conducted in a conventional three-electrode cell. A glassy carbon electrode (GCE) with an area of 0.07065 cm^2 was used as the working electrode, while platinum foil was employed as the counter electrode. The reference electrode was Hg/Hg_2Cl_2 (Saturated calomel electrode, SCE, 0.245 V vs. SHE), which was connected to the cell through a Luggin capillary tip. All the potentials refer to the SCE unless otherwise stated, and the current density was calculated by the geometric area of the GCE. Before the CV tests, all the solutions were deaerated by bubbling high-purity nitrogen (99.9%) for 30 minutes. A typical CV was measured between the potential ranges of -0.5 and 2.0 V at a given sweep rate (10, 20 or 50 mV/s) with a computer-aided potentiostat (Autolab PG30). The impedance response was determined using Pine Research Instrument (Model: AFMSRCE). Since the electrolyte showed a large resistance, IR compensation was performed after cyclic voltammetry. In all of the experiments, stable voltammetry curves were recorded after scanning for 5 cycles.

2.3. Physical characterizations

2.3.1. FT-IR characterization

The FT-IR absorption spectra of the ferric ions in the reline DES were recorded on Vertex 70Hyperion 1000 (Bruker) with a resolution of 4 cm^{-1} and a spectral range of 400-4000 cm^{-1}.

2.3.2. Viscosity measurement

Viscosity measurements were conducted with a viscometer (Shanghai Pingxuan). The reline DES was contained in a tank with the temperature controlled by the water bath. At each temperature point, the viscosity was measured three times and the average was taken.

2.3.3. Conductivity measurement

An electrical conductivity meter (OAKTON Acorn series) was applied to measure the electrical conductivity of the reline DES electrolyte at each given temperature. The electrical conductivity was measured three times and the averaged value was taken.

2.3.4. Solubility measurement

The equilibrium solubility at a given temperature was determined by the shake flask method. The ferric chloride is added in surplus to the reline DES and shaken for 1 hour. The saturation is confirmed by observation of the presence of undissolved material. A sample for analysis was taken after filtration of the slurry. The amount of solute contained in the sample is determined by the gravimetric method.

3. Results and discussion

3.1. Characteristics of the Fe(II)/Fe(III) redox reactions on a GCE

Before testing the CVs of Fe(II)/Fe(III) redox reactions, the CV of the blank reline DES was measured at room temperature, as shown in Fig. 1. The result shows that in the range of -0.8 V to 1.1 V (vs. Hg/Hg_2Cl_2), there is no peak for the oxidation or reduction reaction, which indicates that the DES could provide a wider potential

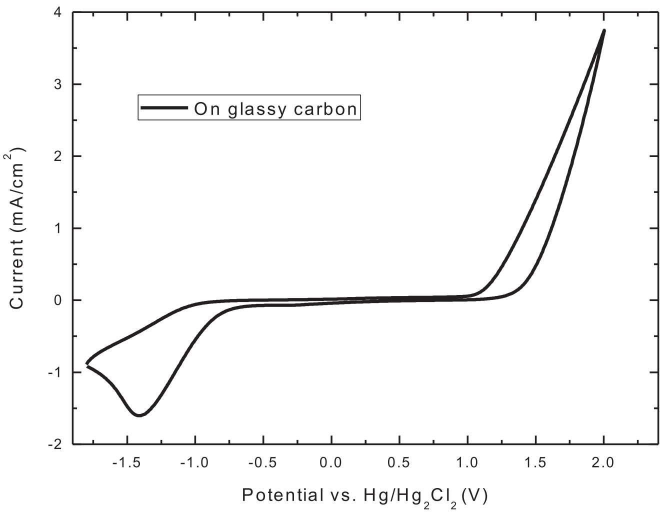

Fig. 1. CV of blank reline DES.

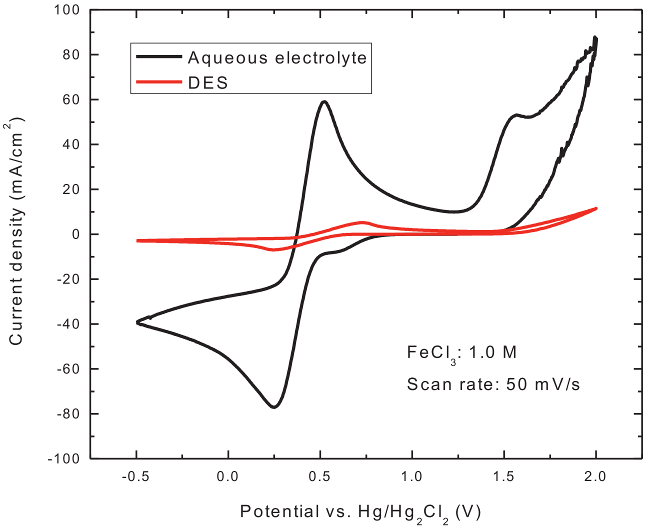

Fig. 2. CVs of 1.0 M $FeCl_3$ in reline DES and in aqueous.