



Kinetics study of transition metal complexes (Ce–DTPA, Cr–DTPA and V–DTPA) for redox flow battery applications

Portia Modiba^{a,b,*}, Mangaka Matoetoe^c, Andrew M. Crouch^d

^a University of Stellenbosch, Department of Chemistry, Private Bag 1, Matieland, Stellenbosch, 7602, South Africa

^b University of Glasgow, Department of Chemistry, Joseph Black Building, Glasgow G12 8QQ, United Kingdom

^c Cape Peninsula University of Technology, Department of Chemistry, P.O. Box 652, Zonnebloem 8001, South Africa

^d University of the Witwatersrand, Faculty of Science, Private Bag 3, Johannesburg 2050, South Africa

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ABSTRACT

Electrochemical kinetics of Ce(IV), Cr(III) and V(IV) and their diethylenetriaminepentaacetic acid (DTPA) complexes are studied by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) on Pt-electrode. Kinetic parameters such as potential, limiting current, transfer coefficient, diffusion coefficients, and rate constants were examined. The EIS results confirm the results from CV and are in good agreement with the obtained experimental data. The Cr–DTPA complex rate constant of $2.1 \times 10^{-4} \text{ cm s}^{-1}$, diffusion coefficient of $1.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and the V–DTPA complex rate constant of $2.2 \times 10^{-4} \text{ cm s}^{-1}$ and diffusion coefficient of $4.9 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ were obtained and compared with the Ce(IV)–DTPA complex. The Ce(IV)–DTPA complex appear to better satisfy the requirement of a suitable electrolyte for RFB applications than Cr(III)–DTPA and V(IV)–DTPA complexes.

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1. Introduction

Energy storage is a main concern today, and the demand for power energy is globally increasing every year. Due to a constantly population growth, the world is facing new challenges in the energy sector. Research in the development of battery technology has been lacking for a long time, and a lot has been ignored decades, particularly in the electrochemistry area. Today researchers have the potential to increase the flexibility of power energy systems and to improve on the response to a sudden demand of energy. The need to meet the growing energy demand will require innovation, such as energy production and storage that will be environmentally friendly.

The redox flow battery (RFB) system has been an active field of research and has been investigated by most researches in recent past years. The first study of RFB was reported by Thaller [1] who used the mix of Fe(II)/(III) and Cr(II)/(III) redox couples for the RFB energy storage system. Later Johnson et al. [2] studied the Fe–Cr redox system on the carbon felt electrode. Afterwards several energy storage technologies were investigated and developed [3–16]. Some technologies have reached the top level but

only a few have become commercially available. More attention is required to develop new energy storage for the next generation. Most researches have been trying to advance the RFB, since it offers great promise as long life, reliable, simplicity, low maintenance and higher efficiency for large scale in energy storage system for a wide range of application [2,4,8,14–28]. A variety of redox couples have been previously used as an electrolyte for redox flow batteries [2–7,13–29]. Some redox couples still suffer from a lower cell voltage and a smaller energy storage capacity, and some have higher voltage but poor reversibility [3,4].

Recently, more attention has been focused on the all-vanadium electrolyte system for RFB [2–7,13,15–19] due to its various advantages. There are fewer complications that RFB encountered, that is, mixing of electrolyte, and chemical degradation due to corrosion. Skyllas-Kazacos and co-workers [2–7,16–19] first introduced the all-vanadium for RFB system, with the idea of solving electrolyte cross contamination, using the same solution for all cells. For this reason there will be no capacity loss caused by the cross mixing of the positive and negative electrolyte during charge and discharging process. Chakrabarti et al. [13] reported that the performance of the all-vanadium system was significantly better than an all-chromium system, though they did observe cross-contamination of active electrolytes. Doria et al. [14] used an all-chromium redox system (Cr(II)/Cr(III) and Cr(III)/Cr(VI)) in a chloride medium for redox flow battery applications, and proposed slow kinetic reactions for both chromium couples. Bae et al. [15] investigated chromium

* Corresponding author at: University of Glasgow, Department of Chemistry, Joseph Black Building, Glasgow G12 8QQ, United Kingdom. Tel.: +44 141 330 8233; fax: +44 141 330 4888.

E-mail address: portiam@chem.gla.ac.uk (P. Modiba).

couple with the addition of EDTA ligand. They found that the redox reaction of Cr(III)–EDTA/Cr(II)–EDTA couple had higher energy output and longer life than a conventional Fe–Cr redox system. However the kinetic reactions of Cr(V)–EDTA/Cr(III)–EDTA was slow.

The complexes of metals with aminopolycarboxylic acid have received considerable attention in recent years, because of the wide application in batteries [8–12,15], super analytical applications [30–42], conductors, electrochemical devices [37,43–45], waste water treatment [43], industrial and agricultural [43,46]. The oxidation of different organic compounds using carboxylic acids with Ce(IV) have been studied extensively and are becoming interesting at present [8–12,30]. Modiba and Crouch [8] first reported the Ce(IV)–DTPA complex as a suitable electrolyte for a single cell RFB system. Afterwards, Modiba and Crouch [9] the Ce(IV)–DTPA complex has been established and compared with Ce(IV)–EDTA complex, uncomplex Ce(IV) and vanadium. The Ce(IV)–DTPA was found to have a higher open voltage circuit potential than the vanadium system after charging. We also reported [10] the charge/discharge performance of Ce(IV)–DTPA complex, and compared these with Ce(IV) in the presence of various aminopolycarboxylic acid (NTA, EDTA and EDDS). The Ce(IV)–DTPA complex was found to satisfy an important requirement for RFB electrolyte.

Fang et al. [23] investigated the Ce(IV)/Ce(III) couple, which has a standard reduction potential of 1.74 V, higher than for all-vanadium RFB. Paulenova and Creager [26] evaluated the cerium couple in the RFB because of its larger positive redox potential, and the cell voltage was predicted to be approximately 1.9 V. Kiekens et al. [28] reported on the cerium system using various electrodes on different electrodes. Liu et al. [29] proved that vanadium can be replaced by cerium in RFB applications by increasing the concentration of sulphuric acid the cerium solution. Abbaspour and Mehrgardi [30] investigated the electrochemical behaviour of Ce(III) ions in the presence of EDTA. The kinetic parameters that transfer coefficient and rate constants for electrocatalytic oxidation of nitrite ion were determined.

Overall the new battery technologies that are currently under development [8–12,23,24,26–28] fluctuate in the use of the Ce⁴⁺/Ce³⁺ redox couple. The Ce⁴⁺/Ce³⁺ redox couple is attractive for RFB technology because of its large positive redox potential, which should result in a battery with a higher cell voltage and a greater energy storage capacity. Pletcher and Valder [27] reported the electrochemical behaviour of the Ce⁴⁺/Ce³⁺ redox couple in aqueous nitrite media, and the electrochemistry of the Ce⁴⁺/Ce³⁺ couple in sulphuric acids solution, which have been widely investigated by most researchers [8–12,23–29].

A cerium couple is the most uncomplicated electrolyte for redox batteries providing a relatively inexpensive and reliable power source. Although production of cerium batteries is generally simple and poses only relatively little environmental impact, various disadvantages of cerium redox batteries persist. To reduce those disadvantages, and improve the ratio of power to weight, alternative ligands can be used to complex cerium with aminopolycarboxylic acid ligand such as DTPA to reach an improved power level.

There are only a few complications that RFB has encountered thus far, namely, mixing of electrolytes, and chemical degradation due to corrosion. It is very important to understand kinetics and thermodynamics of electrolyte for redox flow batteries in order to be able to identify a suitable electrolyte that offers high potential, high current and electrochemical reversibility to the reaction, without the cross contamination of electrolytes. In several cases, the thermodynamic properties of other metal complexes have also been examined electrochemically [26–30,42–44]. However in some cases the influence of complexation on the thermodynamic

properties has not been competently comprehensible, because of the complicated mechanism of the complexation in the reaction that is taking place during the whole process.

Cerium complexes of DTPA have been investigated [8–12] and found to be a suitable electrolyte for redox flow battery. Therefore it was most desirable to study further other metal species chelating tendencies of DTPA ligand and compare them with cerium–DTPA complex. Thus, electrochemical measurements of various metal complexes with DTPA were conducted to examine an appropriate electrolyte for RFB applications. It was challenging to clarify the reaction between metal and ligand, given that they react in a different way with different metal species, and the formation of complexes is different. However, by using CV and EIS it is possible to compare and select the suitable electrolyte that will be more suitable for RFB applications.

2. Experimental

2.1. Materials and reagents

All reagents were of analytical reagent grade unless stated otherwise. Diethylenetriaminepentaacetic acid DTPA were obtained from (Fluka-Riedel-de Haen) sulphuric acid, sodium hydroxide, were purchased from Sigma–Aldrich (Steinheim, Germany), cerium(IV) sulphate [Ce(SO₄)₂], chromium sulphate Cr(III) sulphate Cr₂(SO₄)₃, ammonium vanadate (NH₄VO₃), vanadium vanadate (V₂SO₅), vanadium vanadyl (VOSO₄), were all purchased from Sigma–Aldrich (Steinheim, Germany).

2.2. Preparation of various metal species with DTPA

Chromium (III) sulphate Cr₂(SO₄)₃, ammonium vanadate (NH₄VO₃), Cr–DTPA was prepared as described in the literature [8,48]. The preparation of Cr–DTPA, the EDTA was replaced by adding DTPA, as per literature method, and dissolved in 1 M H₂SO₄. The solution was filtered, and poured in a small designed cyclic voltammetry glass cell. Deionized water was prepared by passing distilled water through a Millipore (Bedford, MA, USA) Milli Q water purification system [8].

2.3. Instrumentation

Cyclic voltammetry (CV) measurements were performed using a BAS 100B voltammetric System from Bio-analytical Systems, Inc., West Lafayette, Indiana, USA. Electrochemical impedance spectroscopy (EIS) measurements were recorded with VoltaLab PGZ 402 (Radiometer Analytical France).

2.4. Electrochemical measurements

Studies were performed using cyclic voltammetry and electrochemical impedance spectroscopy. A three electrode system was used to carry out all electrochemical experiment, platinum electrode with a diameter of 3 mm as a working electrode, Ag/AgCl (3 M NaCl type) as a reference electrode and a platinum wire as a counter electrode.

Impedance measurements were performed in the frequency range from 100 kHz to 100 mHz at potential step from 800 mV to 1300 mV with an applied amplitude of 10 mV. All experiments were performed at room temperature and EIS results were recorded using platinum as working electrode. Alumina micro-polish and polishing pads (Buehler, IL, USA) were used for polishing the electrode. The electrodes were sonicated for 15 min in water, followed by air-dry.

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