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Electrochemical behavior of carbon paper on cerium methanesulfonate electrolytes for zinc-cerium flow battery

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A B S T R A C T

The voltammetric behavior of the Ce(III)/(IV) half-cell reaction in various electrolytes containing 0.6 M Ce was investigated on both pristine and metal-modified carbon paper (CP) electrodes at three different temperatures (25, 40 and 55 °C) in order to find the most favorable electrochemical conditions. The pristine CP displayed robust electrochemical performance for up to 200 repetitive CV cycles while the Pt loaded electrode's performance was stable for only 70 cycles, even though the latter exhibited a more reversible behavior, moving from a quasi-reversible to a reversible system ($D_{ox.} = 4.0 \times 10^{-6}\,cm^2\,s^{-1}$ and $D_{red.} = 2.5 \times 10^{-6}\,cm^2\,s^{-1}$). The In and La metal modified electrodes did not show any improvement with regard to the kinetics or reversibility of the reaction. The addition of 1 M H_2SO_4 to the base electrolyte enhanced the cerium reduction reaction by a factor of 3, ($-7.2 \times 10^{-3}\,A\,cm^{-2}$). The highest exchange current densities (j_o) were achieved at 40 °C for the CP-Pt ($1 \times 10^{-3}\,A\,cm^{-2}$) attributable to the presence of the catalytic Pt. Elevated temperatures (40 and 55 °C) improved D and $\Delta E_{p.}$ while also the mass transport parameters a) dynamic viscosity (~1.5 mPa·s) and b) electrolytic conductivity (~265 mS cm^{-1}) of the Ce (III)/(IV) half-cell reaction. Overall, pristine CP and to a lesser extent CP-Pt demonstrated good stability with prolonged cycling and kinetics comparable with the ones of Pt and Pt based electrodes.

1. INTRODUCTION

Redox flow batteries (RFB) are among the leading energy storage technologies for the future because of their lower operating cost, scale-ability and versatility. These batteries are able to store large quantities of energy and have the potential to increase the flexibility of power systems and improve the response to the rising energy demand while minimizing environmental damage, where they can be used as a rapid response storage medium and hence facilitate load leveling. RFB can also be applied for use with renewable energy sources, such as solar and wind. Examples of this system include the all-vanadium [1], vanadium-cerium [2], bromine-polysulfide [3], vanadium-polyhalide [4], vanadium-bromine [5], soluble lead-acid [6] and the recently developed zinc-cerium [7–9] RFB. A number of reviews on RFB systems have been published highlighting the increasing interest in this type of energy storage [10–14].

At the negative electrode of the zinc-cerium cell, during charging the metal ions move from the solution and deposit onto the electrode ($Zn(II) + 2e^{-} \rightarrow Zn$, $E^{\circ} = -0.76$ V vs S.H.E) [15,16] whereas at the positive electrode, oxidation of the Ce(III) to Ce (IV) occurs as the primary reaction ($Ce^{3+} \rightarrow Ce^{4+} + e^{-}$, $E^{\circ} = 1.44$ V vs S.H.E), giving a thermodynamical open circuit potential for the cell of 2.2 V vs S.H.E, the highest amongst all RFB systems. Ce(IV) is a strong one-electron oxidant under acidic conditions but stable under alkaline. Ce(III) on the other hand gets oxidized by atmospheric oxygen. Due to the high standard potential of the Ce(III)/(IV) couple (1.44 V *vs* S.H.E in 1 M H2SO4) where $E^{\circ}_{Ce(III)/(IV)}$ strongly depends on the acidity of the solution and the nature of the counter ion [17]), the oxygen evolution reaction (OER: 2H2O $\rightarrow 4H^{+} + 4e^{-}$ + O2) takes place in parallel as the E°_{OER} is 1.23 V. For this RFB system, methanesulfonic acid (MSA) is used as a common electrolyte due to the fact that it allows both zinc and cerium electroactive species to dissolve at concentration larger than 0.8 M [10,18]. MSA has a relatively low toxicological risk potential ($LD_{50} = 1000\,mg\,kg^{-1}$) [10,19]. In the study of Leung [20], the optimal solubility and thus concentration region for Ce(III) and Ce(IV) with regards to MSA were investigated and defined. Also along these lines, the review article of Xie [21] discussed the most significant developments and challenges of the cerium half-cell including electrolyte compositions and the complex chemical reactions.

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Previous studies on the cerium redox couple have examined the kinetics of the reaction on Pt and Pt-Ir electrodes that have undergone various pretreatments such as etching, sandblasting and heat treatment [18,22]. The outcome of these studies showed that Pt-Ir coatings containing larger amounts of Pt exhibited the largest exchange current density at 60 °C and appeared best suited for use as the positive electrode in the Zn-Ce RFB. Currently, for the zinc-cerium RFB, the negative electrode is usually a PVDF or PVE carbon composite, while for the positive electrode a Pt-Ti mesh ($10\,g\,m^{-2}$ Pt) is commonly used [10].

Recently, the introduction of mixed acid media has been introduced in several RFB systems improving the reaction kinetics and energy density [13,14,23]. Regarding the cerium reaction, a recent study by the authors on cerium containing mixed acid electrolytes (4 M MSA + 0.5–2 M HCl, H2SO4 or HNO3) reported a substantial enhancement in the kinetics and the reversibility, especially in the presence of 0.5 M HCl along with 4 M MSA and 0.6 M Ce on a Pt disk electrode [24].

Carbon paper (CP), which consists of micrometer-sized carbon fibers, has found applications in a variety of fields such as fuel cells, biological sensors and lithium-ion batteries due to its high porosity and surface area, permeability and strength along with low electrical resistivity [25,26]. Besides, it can be relatively easy prepared and modified. For instance, a simple dip coating process followed by heat treatment in air is an environmentally friendly way to improve power production in RFB systems by increasing the surface area. Other treatment methods frequently used in CP electrodes include acid treatment, for example soaking in sulfuric acid as well as the addition of surface coatings, mainly metals such as Au or In [27].

In this half-cell study, pristine and metal modified carbon paper (CP) electrodes being a) cost-effective and b) easier to handle and modify than Pt, Pt-Ti or Pt-Ir based electrodes are investigated in the presence of mixed/unmixed cerium methanesulfonate electrolytes in order to determine their suitability for RFB applications.

2. EXPERIMENTAL DETAILS

A standard 3-electrode configuration was employed using platinum wire (CH Instruments) as the counter electrode and either Hg|Hg2SO4|K2SO4 (sat.) or Ag|AgCl as the reference electrode, with potential of 0.64 V and 0.237 V vs S.H.E, respectively. The potential (E/V) axis in all the CV's and kinetic figures has been corrected for and measured against S.H.E. The electrolyte was contained in a jacketed cell, which enables a temperature control of ±1 °C by means of a thermostatic water bath. All solutions were prepared using Milli-Q deionized water (resistivity 18.2 MΩ cm): MSA (99%, International Laboratory USA), sulfuric acid (95–97%, Sigma Aldrich), nitric acid (99%, International Laboratory USA), hydrochloric acid (37%, Sigma Aldrich) and cerium carbonate (99.9% REO, International Laboratory USA). For the metal modification of the carbon electrodes, lanthanum (III) oxide (99.9%, Sigma-Aldrich) and indium (III) chloride tetrahydrate (97% Sigma-Aldrich) were used.

The concentrations of both oxidized and reduced species were measured through colorimetric redox titration (the indicator used to evaluate the Ce(IV) concentration, was a 1:10 phenanthroline–ferrous–sulfate complex solution titrated against standardized ferrous ammonium sulfate) [28]. The electrolytic and thermal conductivity of the cerium solutions was measured by a Mettler-Toledo SevenMulti^{TM} S40 high performance pH/mV/°C Meter and a C-Thermal TCi^{TM} Thermal conductivity analyzer respectively, while the dynamic viscosity was determined by a NDJ-9SB Digital Viscometer (Shenyang Faith Trading Co. Ltd).

The CP electrodes (Shanghai Hesen Electric, thickness: 30 mm, ohmic resistance: $0.1\,cm^2$, in plane conductivity: $1.16\times10^{-6}\,\Omega\,cm^{-2}$, porosity: 75%) having a geometrical surface area of $0.6\,cm^2$ were firstly immersed in ethanol for 20 min and then dried in air. Then, they were immersed in the metal containing solution (two different concentrations were investigated, 0.05 and 0.1 M) in 1 M HCl (37%, Sigma Aldrich) for 1 hour. Afterwards, the CP samples were subjected to heat treatment at a carbonization rate of $5\,°C\,h^{-1}$ for 3 hours at 450 °C. The dip coating method followed by thermal treatment was not implemented for the CP-Pt electrode. The latter was supplied by Toray Industries and used as received (Porosity: 80%, thickness: 23.5 mm, through plane resistance ($m\Omega\,cm^2 < 12$), Pt loading: $0.8\,mg\,cm^{-2}$). The electrical conductivity of the samples prior to and after experimentation was measured using the 4-point probe technique through a Keithley 2400 SourceMeter [29].

The cyclic voltammograms, polarization resistance and Tafel plots were performed using a ZAHNER-IM6 electrochemical workstation. The wettability of the electrode surface was evaluated

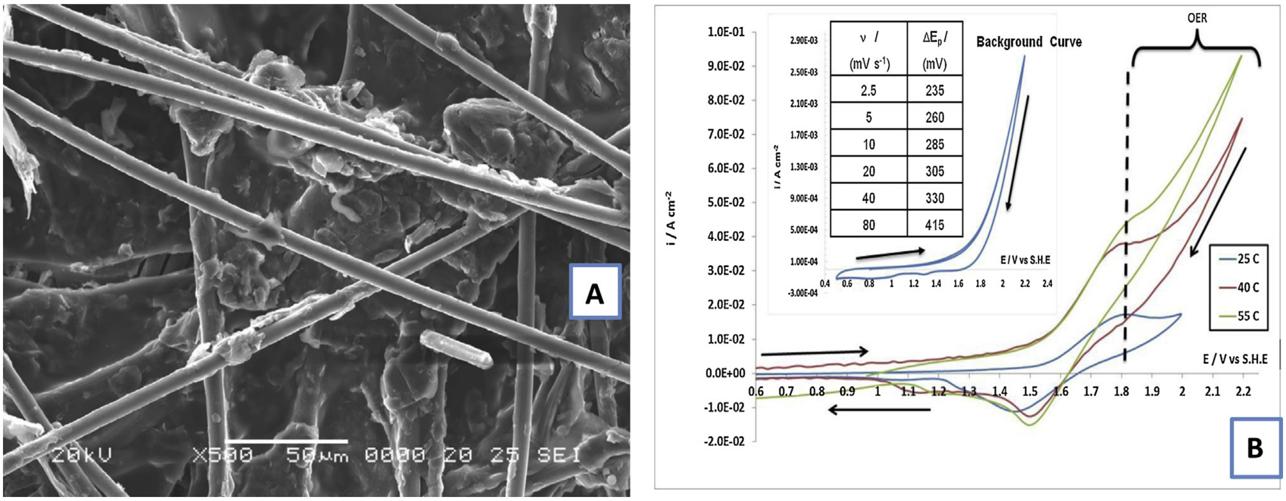

Fig. 1. (A) SEM micrograph of pristine carbon paper, magnification ×500 at 20 kV (B) Cyclic voltammograms at different temperatures on a pristine CP ($0.6\,cm^2$) electrode in 0.6 M cerium carbonate hydrate (3H$_2$O) and 4 M MSA. Scan rate = $5\,mV\,s^{-1}$. Inset shows the peak-to-peak separation (ΔE_p) of the cyclic voltammogram at 40 °C and the background curve at that temperature and scan rate ($5\,mV\,s^{-1}$). Above $10\,mV\,s^{-1}$ ΔE_p is greater than 59 mV and increases with elevated scan rates (ν) suggesting a quasi-reversible system.