

# SUBSTRATES FOR THE POSITIVE ELECTRODE REACTION IN THE ZINC-CERIUM REDOX FLOW BATTERY

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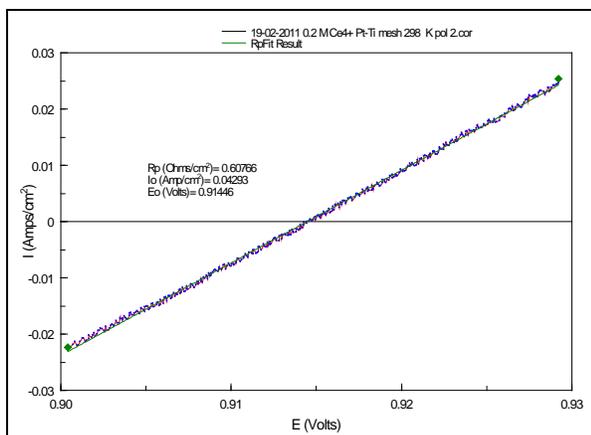
## ABSTRACT

The key to maintaining the high open circuit values of the zinc-cerium redox flow battery during charge and discharge is to minimize the overpotential losses by careful choice of electrodes and current densities employed as well as cell design. This study examined the positive electrode reaction on a variety of electrode substrates consisting of coatings of platinum, platinum/iridium, and titanium/tantalum on titanium substrates as well as commercial DSAs in order to assess the electron transfer kinetics of the  $\text{Ce}^{3+}/\text{Ce}^{4+}$  reaction and so allow benchmarking for future developments to take place.

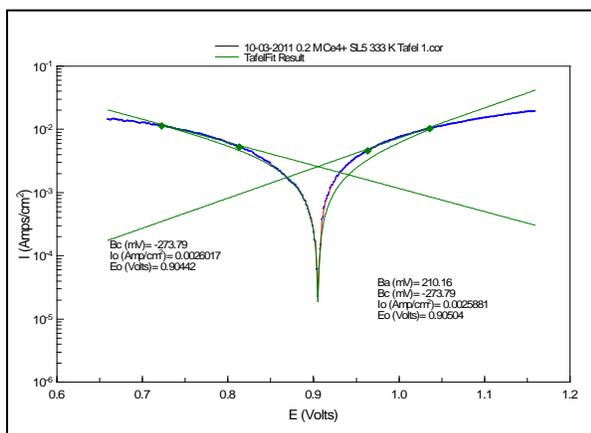
The zinc-cerium hybrid redox flow batteries (RFBs) [1] have one of the largest open circuit values (~2.4 volts) of any current RFB system. The key to maintaining this as high as possible during charge and discharge is to minimize the overpotential losses by careful choice of electrodes and current densities employed as well as cell design. In this study, the positive electrode reaction, i.e.,  $\text{Ce}^{4+} + \text{e}^- \rightleftharpoons \text{Ce}^{3+}$ , was examined on a variety of electrode substrates consisting of platinum (Pt), platinum/iridium (Pt/Ir), and titanium/tantalum (Ti/Ta) as well as commercial DSAs in order to assess the electron transfer kinetics and so allow benchmarking for future material developments to take place. The experiments were performed over the temperature range 24 °C to 60 °C in methane sulphonic acid (MSA) as the base electrolyte with the cerium concentration set at 0.8 M. The techniques of cyclic voltammetry, Tafel extrapolation, polarization resistance, electrochemical impedance spectroscopy (EIS), as well as rotating disk (RDE) techniques were employed in order to assess the performance of the different electrocatalytic coatings for the  $\text{Ce}^{3+}/\text{Ce}^{4+}$  reaction.

For the electrode substrates employed, it was important that the available electroactive surface area was correctly determined and for this, both the underpotential hydrogen evolution reaction and

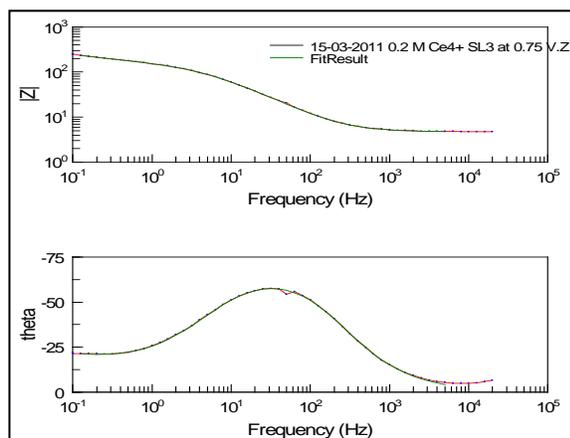
carbon monoxide adsorbed layer oxidation regions in 1.0 M sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were employed [2,3]. For a geometric area of 1 centimeter squared ( $\text{cm}^2$ ), the electroactive areas for the coated samples were found to be in the range of 75  $\text{cm}^2$  to 125  $\text{cm}^2$ , depending on the preparation procedure. Typical results from polarization resistance and Tafel extrapolation measurements obtained from the samples are shown in Figures 1 and 2, respectively. Exchange current densities were in the range  $1.7 \times 10^{-6} \text{ A cm}^{-2}$  to  $1.0 \times 10^{-4} \text{ A cm}^{-2}$  for the Pt-Ir catalysts and between  $2.0 \times 10^{-7} \text{ A cm}^{-2}$  and  $9.5 \times 10^{-5} \text{ A cm}^{-2}$  for the sole Pt-based respectively. Ta-based electrodes seemed to inhibit the oxygen evolution process but the electrochemical kinetics for the oxidation of Ce(III) and the subsequent reduction of Ce(IV) were also correspondingly very slow ( $\sim 10^{-7} - 10^{-8} \text{ A cm}^{-2}$ ). Exchange current densities on the iridium-oxide-coated electrodes were between  $3.5 \times 10^{-5} \text{ A cm}^{-2}$  and  $8 \times 10^{-5} \text{ A cm}^{-2}$ . However, for all the range of substrates investigated, an increase in temperature to 60 °C favored the kinetics of the  $\text{Ce}^{3+}/\text{Ce}^{4+}$  reaction as higher exchange current densities were recorded. EIS measurements were also conducted on the substrates at 25 °C (Figure 3) and the data obtained were in good agreement with the data from the above two other techniques.



**Fig. 1. Polarization resistance on Pt-Ti mesh electrode at 298 K. Scan rate: 0.1667 mV s<sup>-1</sup>.**



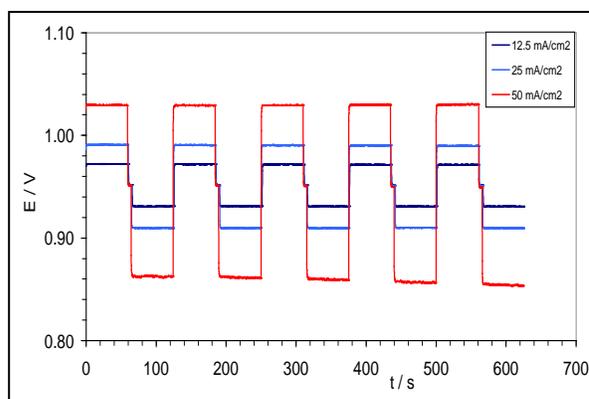
**Fig. 2. Tafel analysis on Pt-coated electrode (3 g cm<sup>-2</sup> of Pt) at 333 K. Scan rate: 2 mV s<sup>-1</sup>.**



**Fig. 3. Impedance data at halfwave potential (0.75 V) on Pt-coated electrode (5 g m<sup>-2</sup> etched) at 298 K.**

Under the flow regimes used, charge-discharge cycles on the Pt disk and Pt/Ti mesh electrodes revealed as expected 100% coulombic efficiencies in a solution consisting of 0.2 M Ce<sup>4+</sup> in 6.9 M MSA at current densities <100 mA cm<sup>-2</sup> (Figure 4). However, at higher current densities, the sharp increase in potentials suggest that oxygen (during charging) and hydrogen (during discharge) evolution reactions are occurring with resulting loss in current efficiency at these electrodes.

Data will also be presented for the complete Zn-Ce hybrid RFB where the overall current, voltage, and energy efficiencies as a function of current density are determined during multiple charge-discharge cycles.



**Fig. 4. Galvanic cycles at different charge current densities under solution flow in 0.2 M Ce<sup>4+</sup> in MSA - 333 K -Pt-Ti mesh (Geometric area: 4 cm<sup>2</sup>).**

## REFERENCES

- [1] [http://plurionsystems.com/tech\\_flow\\_technology.html](http://plurionsystems.com/tech_flow_technology.html).
- [2] T. Biegler, D.A. Rand, R. Woods, "Limiting oxygen coverage on platinumized platinum; Relevance to determination of real platinum area by hydrogen adsorption," *J. Electroanal. Chem.* **29**, 1971, pp. 269-277.
- [3] R. W. Lindström, K. Kortsdottir, and G. Lindbergh, "Active area determination for porous Pt-electrodes used in PEM fuel cells. Temperature and humidity effects." *Applied Electrochemistry*, School of Chemistry and Engineering, KTH Royal Institute of Technology SE-10044 Stockholm, Sweden.

## BIOGRAPHICAL NOTE



**Conference presenter:** Dr Len Berlouis is a Reader in Physical Chemistry in the Department of Pure and Applied Chemistry at the University of Strathclyde, Glasgow, Scotland. He obtained his Ph.D. from Southampton University (England, UK) in 1982 working on AC impedance characterization of flow-through porous electrodes. He then worked as a research scientist at the Wolfson Centre for Electrochemical Science (Southampton) for 9 years on projects ranging from electropolymerisation, corrosion studies, sensors, semiconductor electrochemistry, and interfacial spectroelectrochemistry. He moved to the University of Strathclyde in 1991, and since then he has extended his work involving optical techniques (ellipsometry, electrolyte electroreflectance, and second harmonic generation ([SHG]) for characterizing solid/electrolyte interfaces. This led to a number of publications as well as presentations (orals and posters) at international conferences. In more recent years, the technique of SHG in particular was extensively used to examine the surfaces of

epitaxial semiconductor single crystals and the effect of mismatch between the substrate and the epitaxial layer. The adsorption of small molecules/atoms at single crystal metal surfaces (e.g., platinum, gold) was also followed with these techniques as well as changes in surface symmetry and reconstruction as a function of applied potential. Here, the electroreflectance technique as well as surfaced enhanced Raman scattering (SERS) were employed to good effect. He has been an active researcher in redox flow battery systems for the last three years working in close collaboration with Plurion Ltd., Glenrothes, Scotland, as well as colleagues from the University of Southampton, England, and has presented this work at major international conferences.

He has over 70 peer-reviewed publications and has had active international collaborations with the Electrochemistry Groups at the École Polytechnique Fédérale de Lausanne (Switzerland), the Department of Physical Chemistry, University of Alicante (Spain), the Laboratoire de Spectrométrie Ionique et Moléculaire at the Université Claude Bernard, Lyon (France), the Solidstate Physics Laboratory, Delhi (India) and SRI International, Menlo Park, California.

