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A Novel Regenerative Hydrogen Cerium Fuel Cell for Energy Storage Applications

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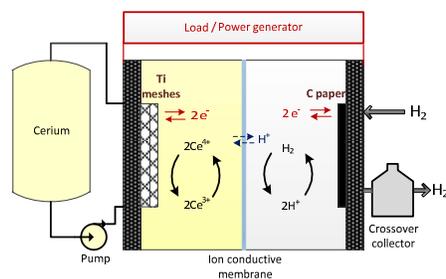
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A novel regenerative hydrogen cerium fuel cell is presented which has the potential to deliver both low cost and high performance. A 5 cm² prototype is demonstrated, achieving 148 mW.cm⁻² when fully charged. Rate determining processes within the cell are identified.

A global target has been set to reduce greenhouse gas emissions by 40% to 70% by 2050 compared to 2010 levels.¹ However energy generation from renewable sources suffers from their intermittent and unreliable nature. Hence large-scale energy storage has become a vital technology in order to meet the set targets, e.g. through the development of smart grids.²

Electrochemical energy storage devices are one of the most efficient ways of converting and storing electrical energy. Out of many options, redox flow batteries (RFBs) or regenerative fuel cells are one of the most promising for large scale energy storage, especially for high energy applications. They have the ability to convert chemical energy into electrical energy; often referred to as reversible or regenerative fuel cells, they typically utilise two soluble redox couples contained in separate electrolyte tanks external to the battery. Each electrolyte is pumped through their respective half-cell such that energy is stored/released as the RFB is charged/discharged.³ These two half-cells are separated by an ion exchange membrane that selectively allows ions to pass from one electrolyte to the other, with the electrons passing through an external circuit.⁴ The crucial requirements for grid level energy storage applications are all met by RFBs, namely fast response time (~milliseconds), site independence, low environmental footprint,

high depth of discharge, high reliability, high round trip efficiency (ca. 85%) and long life cycle (>>13 000 cycles).⁵⁻⁷ Additionally, they are highly modular as the electrolyte volume and concentration determine the energy of the system, while the power depends on the stack size and the active surface area of each cell⁸, hence RFBs are used for a wide range of energy storage applications.

A large number of redox couples has been investigated in RFB research such as Fe/Cr, Poly-Sulphide/Br₂, Zn/Cl₂, Zn/Ce, all-vanadium redox battery (VRB), V/Ce and Zn/Br₂.⁵ However, only the VRB and the Zn/Br₂ systems have been developed to a commercial level, and are currently exploited in applications such as load levelling, power quality control, and solar and wind deployment.⁹

Recent developments in RFB research has shown increasing interesting redox couple combinations that deliver high cell voltage and hence high energy density systems.¹⁰ Among them the cerium couple Ce(III)/Ce(IV) has been studied in several solvent compositions; the Zn/Ce RFB initially developed by Plurion Inc. (UK) in 2004 is one of the most popular.¹¹⁻¹⁷ The cerium half-cell reaction, described in Equation (1), offers a high positive voltage of 1.72V vs SHE, however, at such high potentials carbon based electrodes, which are typically used in RFBs, are no longer stable and undergo corrosion.^{13,18}

In parallel to the development of RFBs, years of fuel cell development has led to the development of H₂/metal based RFBs where the hydrogen side is similar to the anode side of a proton exchange membrane fuel cell (PEMFC). The absence of cross-contamination is a major asset of these gas/liquid RFBs, meaning no permanent capacity loss through mixing of anolyte and catholyte. A modified PEMFC using hydrogen and Fe(III)/Fe(II) was investigated by Fatih et al. which later led to the development of a H₂/Fe redox flow cell.^{19,20} Promising performance results have been reported on this system, with power densities of 270 mWcm⁻² and 257 mWcm⁻² for 1M FeSO₄ and 0.9M iron chloride with 0.9M HCl solutions respectively.^{20,21,21} In addition, a H₂/Br₂ system recently demonstrated a peak power density of 1400 mWcm⁻², making it a promising candidate, though concerns remain about the toxicity and associated safety issues in the case of bromine leakage.²³ Another successful hydrogen based RFB was investigated by Yufit et al.

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which combines the V(IV)/V(V) couple from the popular VRB with a hydrogen anode; a promising initial study demonstrated power performance of 127 mWcm^{-2} for an un-optimised system.^{24,25}

Here we report a novel Regenerative Hydrogen-Cerium Fuel Cell (RHCFC) which combines the high voltage cerium redox couple with the hydrogen generation reaction, usually considered as parasitic in other systems.²⁶

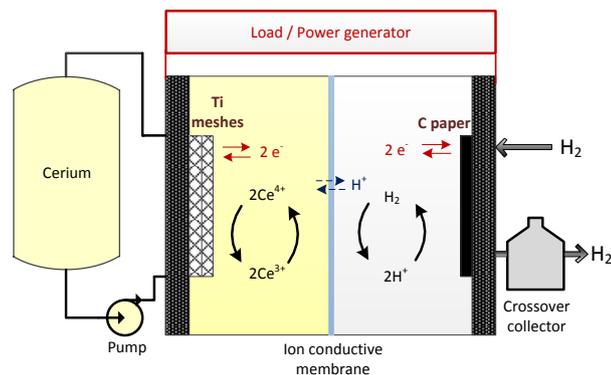
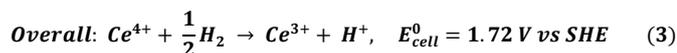
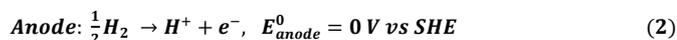
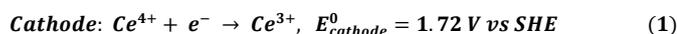


Figure 1: Schematic illustration of the RHCFC.

As represented in Figure 1, a solution of Ce(III)/Ce(IV) is pumped through the cathode whereas hydrogen is passed through the anode. The cathode and anode are separated by a cation exchange membrane that allows protons to pass through while electrons pass through an external circuit. When the cell is in energy delivery mode (discharging) cerium (IV) is reduced to cerium (III) whereas hydrogen is oxidised to protons as described in Equations (1-3):



The experiments were carried out using a single cell assembly that had a 5 cm^2 active area as displayed in Figure 1. Two superimposed platinised titanium meshes (METAKEM G, $700 \mu\text{m}$ thick each) were used as electrodes on the cathode side and a platinised carbon based electrode (Alfa Aesar Hydrogen Electrode, $200 \mu\text{m}$) was used on the anode. The two electrodes were separated by a Nafion® 117 membrane. The electrolytes were pumped through serpentine graphite flow channel plates (SGL PPG85 graphite plates) that also served as current collectors. A plastic based insulating layer (RS polypropylene sheet) was sandwiched by aluminium end plates in order to provide a uniform pressure distribution to the cell and electrical insulation. Viton gaskets were used between the different layers of the cell to provide a good seal. Finally a crossover collector was connected to the hydrogen outlet to collect any liquid electrolyte crossing to the gas side.²⁷

A cerium solution (50 mL) of 0.5M was prepared by adding 5.75 g of Ce (III) carbonate (Sigma-Aldrich) to 38 mL of deionised water and then dissolving the stirred mixture by slowly adding 12 mL of concentrated methanesulfonic (MSA) acid (Sigma-Aldrich) until a clear Ce (III) solution was obtained. The final concentration of MSA was 4M. Using a peristaltic pump (Cole Palmer 77200-50) the catholyte was pumped at 48-146 mL/min depending on the experiment, whereas the hydrogen was flowing through the anode at constant 50 mL/min in all experiments.

Galvanostatic charge/discharge curves were recorded using an Autolab PGSTAT30 with a 10A current booster (Autolab BSTR10A) running NOVA 1.9 software. Measurements were made using a 4-electrode set-up to minimise contact resistance losses of the measurement probes. The hydrogen flow rate was controlled using a Bronkhorst (EL-FLOW) mass flow controller. Figure 2 shows the charge/discharge characteristics of the RHCFC. The upper and lower voltage limits were set to 1.8V and 1.5V respectively as calculated through the Nernst equation (Equation 4) assuming 0.495 and 0.005 M concentration of Ce(IV) and Ce(III) respectively. However it has been seen in literature that E_{cell}^0 for the cerium redox couple may vary between 1.28V to 1.72V due to the change of activity in different solvents.^{28,29}

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{RT}{F} \ln \frac{[\text{Ce}^{4+}] (P_{\text{H}_2})^{0.5}}{[\text{Ce}^{3+}][\text{H}^{+}]} \quad (4)$$

Between experiments, the cell was held at the limits of potential until the current dropped to $< 2 \text{ mA/cm}^2$ in order to measure charge/discharge curves from the same datum. This procedure was not carried out at 5 mA/cm^2 , as the overpotential was so low, the current would drop below the cut-off current density straight away; hence the efficiency calculations were made at this current density. Both, the coulombic efficiency (CE) defined as the ratio of the discharge capacity over the charge capacity, and the voltage efficiency (VE) defined as the average voltage during discharge over the average voltage during charge, were equal to 94%. Thus the energy efficiency (EE), which is the product of CE and VE, was calculated to be 88%, a promising result for the first generation of RHCFC.

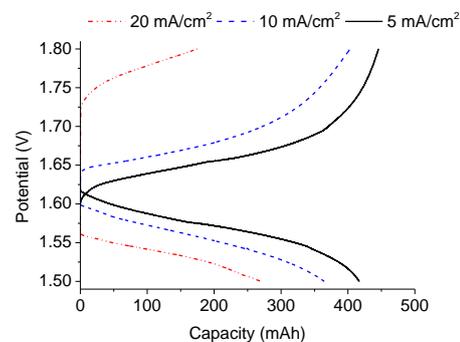


Figure 2: Galvanostatic charge/discharge curves of the RHCFC with a hydrogen flow rate of 50 ml/min and cerium flow rate of 97 ml/min at different current densities.

Observations of the charge/discharge behaviour in Figure 2 shows an asymmetry between the charge and discharge processes, with more available capacity under charge than discharge at low current densities, suggesting that the charge kinetics are faster than the discharge. However, the opposite is true at higher current densities, suggesting that mass transport losses are more significant for the charging processes.

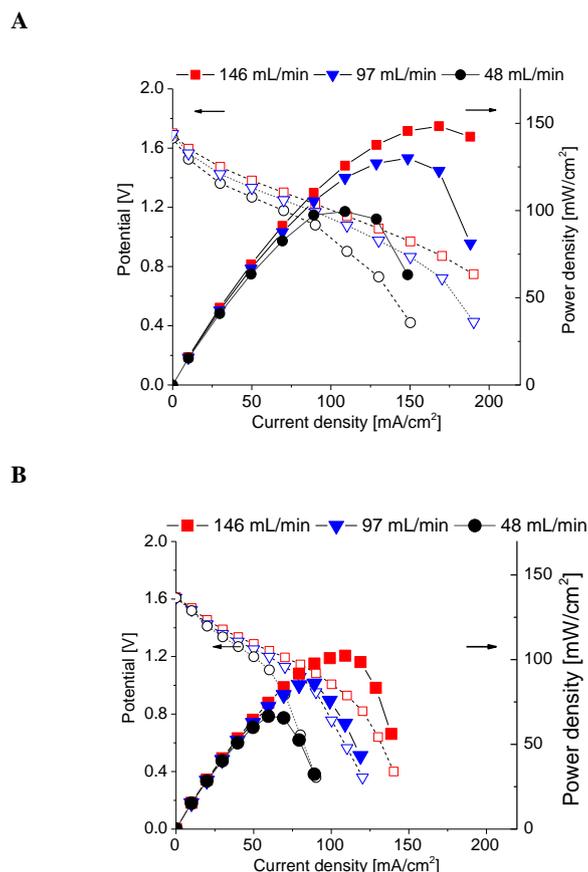


Figure 3: Power curve data taken at A) 100% and B) 50% SOC for different cerium flow rates and at 50 mL/min flow rate for hydrogen.

Power curve data was also taken by applying repeating charge and discharge pulses of 10 s with a 30 s rest in between. This ensured that the state-of-charge (SOC) remained relatively constant during the measurements, and also that concentration gradient from one pulse did not affect the next. The 100% SOC was defined by the fully charged cell at 5 mA/cm².

Comparison between the potential curve at 100% and 50% SOC demonstrated that the initial drop in the potential is larger at 100% than at 50%. This initial potential drop is due to activation overpotential which is related to the charge transfer processes in the cell.

Analysis of the power curve data showed that a peak power density of 148 mW/cm² was achieved at a flow rate of 146 mL/min. It can

times smaller) the maximum power density drops by 12% to 130 mW/cm². At the flow rate of 48 mL/min (3 times less), the peak power density dropped by 32% to 100 mW/cm². A similar behaviour was observed at 50% SOC: at 97 and 48 mL/min flow rates a peak power density drop of 16% and 34% were respectively observed compared to the peak power density achieved at 146 mL/min. Therefore, the peak power is a clearly a function of the cerium flow rate, indicating mass transport limitations. It also demonstrates that a reduction of the cerium flow rate can have a larger detrimental effect on the RHCFC performance than a decrease in SOC.

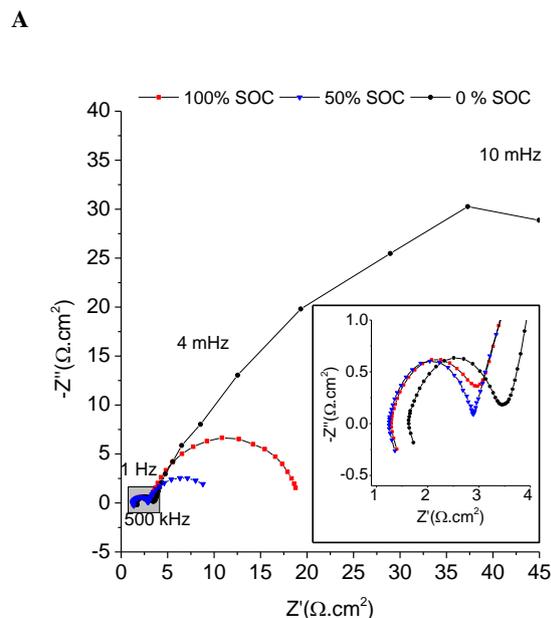


Figure 4: A) Nyquist representation of EIS measurements at different SOC's with a hydrogen flow rate of 50 mL/min and cerium flow rate of 146 mL/min B) equivalent circuit used in order to fit the EIS data.

Electrochemical Impedance Spectroscopy (EIS) measurements were taken from the cell at 100%, 50% and 0% SOC. Measurements were made with a current RMS of 50 mA over a frequency range of 500

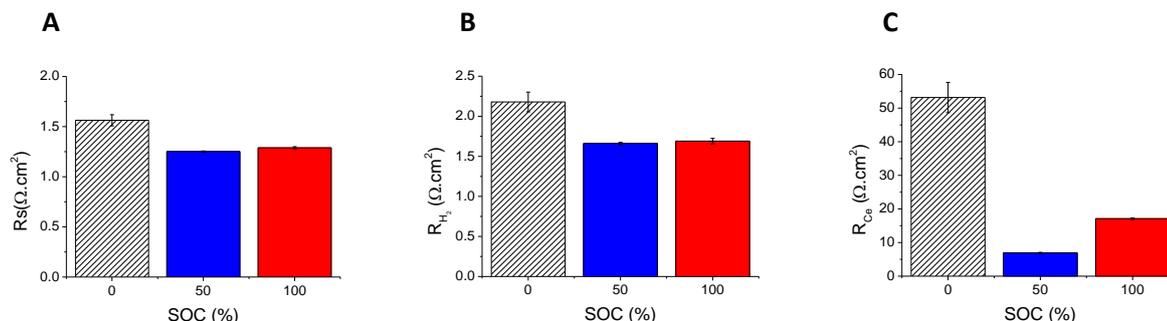


Figure 5: A) Series, B) Hydrogen charge transfer, C) Cerium charge transfer, resistance at different SOC's for a hydrogen flow rate of 50 mL/min and cerium flow rate of 146 mL/min.

be seen that at 100% SOC, at a cerium flow rate of 97 mL/min (1.5 kHz to 0.01 Hz. Figure 4A presents a typical EIS response of the

RHCFC at different SOC. The Nyquist plots in Figure 4A display two depressed semi-circles at all SOC, indicating the presence of at least two different processes in the RHCFC.

While the shape of the EIS spectra appears to be similar at higher frequencies, the resistance at lower frequencies is considerably larger in the fully discharged state. In order to extract quantitative information from the EIS measurements, the data was fitted to the equivalent circuit shown in Figure 4B using ZView software. In this circuit, the inductor L and the resistance R_s represent the inductive response of the electronically conductive components in the cell including current probes and wires, and the series resistance of both electronic and ionic conductive components of the RHCFC respectively. The second element, comprising the constant phase element CPE1 and the parallel resistance R_{H_2} , is attributed to the charge transfer resistance associated with the hydrogen side; this was confirmed after further EIS experiments were carried out at different cerium flow rates where the first semi-depressed circle remained unchanged while the second varied. Therefore the symmetrical third element comprising CPE2 and R_{Ce} is attributed to the charge transfer losses associated to the cerium side. From the values of the fitted data (Figure 5A, B and C), the series resistance appears to be similar between 50 and 100% SOC with only a decrease of 3% from 100 to 50% SOC. The charge transfer resistance of the hydrogen side shows an analogous behaviour, with a decrease of only 2% from 100 to 50% SOC. However at 0% SOC the series resistance and the charge transfer resistance of the hydrogen side is higher by 21 and 29%, respectively, in comparison to 100% SOC. Given that the proton concentration varies from 3M at 100% SOC to 4M at 0% SOC, the higher level of proton concentration in the bulk solution at 0% SOC could lead the Nafion membrane to uptake MSA leading to a decrease of proton mobility, as similar behaviour has been observed for Nafion membrane in a sulphuric acid environment.³⁰ This would explain why the proton concentration would affect both the series resistance and charge transfer resistance of the hydrogen electrode. Finally, looking at the charge transfer resistance of the cerium electrode (Figure 5C), a “U” shape pattern is observed where the losses are the lowest at 50% SOC, which is expected as no one reactant is depleted more than the other. This is also in agreement with the result found in Figure 3A and 3B suggesting a larger charge transfer resistance at 100% than at 50%. In comparison to the resistance of $6.9 \Omega \cdot \text{cm}^2$ at 50% SOC, R_{Ce} rises to $17.1 \Omega \cdot \text{cm}^2$ at 100% SOC and to $53.2 \Omega \cdot \text{cm}^2$ at 0% SOC. The threefold difference in resistance between the fully charged and discharged state highlights further the asymmetry at the different states of charge, that has also been demonstrated through cyclic voltammetry experiments in literature.¹¹ Furthermore it is also believed that the increase in resistance is also partially due to a decrease of proton mobility in the membrane. It is clear from these results that the overall resistance in the cell is largely dominated by the charge transfer losses on the cathode as they are a factor of 10-35 times larger than other source of losses.

Conclusions

The feasibility of a novel regenerative fuel cell combining hydrogen with the Ce(III)/Ce(IV) redox couple has been demonstrated. Successful charge and discharge at different current densities was carried out. A peak power density of 148 mW/cm^2 was achieved at 100% SOC, and its value decreases rapidly with decreasing cerium flow rate. These experiments demonstrated the asymmetry between the charge and discharge processes, where the charging step is mass transport limited on the cerium side. EIS data confirmed that the cell is ultimately limited by kinetic losses on the cerium side where the resistance is higher at 0% SOC than at 100%. It also shows that the series resistance and the charge transfer resistance of the anode is

higher at 0% SOC as the concentration of MSA is higher, perhaps leading to reduced mobility of protons in the membrane. However in order to validate these initial conclusions, further work is necessary to decouple the anode and cathode processes. Furthermore it is clear that this cell was built as a proof of concept. Hence more work will be done to design non carbon based electrode materials that enhance mass transfer rates, as prolonged contact with the cerium electrolyte leads to carbon corrosion due to the high operating potential.

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