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Vanadium proton exchange membrane water electrolyser

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HIGHLIGHTS

- Demonstration and study of a vanadium/water electrolyser.
- High current densities and efficiency during reduction of V^{3+}.
- Localization of IR-losses and optimisation suggestions.

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ABSTRACT

In order to reverse the reactions of vanadium oxygen fuel cells and to regenerate vanadium redox flow battery electrolytes that have been oxidised by atmospheric oxygen, a vanadium proton exchange membrane water electrolyser was set up and investigated. Using an existing cell with a commercial and iridium-based catalyst coated membrane, it was possible to fully reduce $V^{3.5+}$ and V^{3+} solutions to V^{2+} with the formation of oxygen and with coulomb efficiencies of over 96%. The cell achieved a maximum current density of 75 mA/cm^2 during this process and was limited by the proximity of the V(III) reduction to the hydrogen evolution reaction. Due to the specific reaction mechanisms of V(IV) and V(III) ions, V(III) solutions were reduced with an energy efficiency of 61%, making this process nearly twice as energy efficient as the reduction of V(IV) to V(III). Polarisation curves and electrochemical impedance spectroscopy were used to further investigate the losses of half-cell reactions and to find ways of further increasing efficiency and performance levels.

1. Introduction

In power grids that harness renewable energy sources, electrical energy has to be stored in order to bridge supply shortfalls. As a result of this, research into stationary electrochemical storage technologies has intensified in recent years and increasing attempts are being made to commercialise this technology [1–5]. Redox flow batteries [6–12] represent one option here. This technology uses a cell in conjunction with electrochemical reactions to store electrical energy in a liquid solution. The energy can then be recovered using the same cell. Redox flow batteries are similar to fuel cells and electrolysers, whereby the latter two technologies only convert energy in one direction. The vanadium/oxygen fuel cell (VOFC) has evolved from developments to vanadium redox flow batteries [13]. In VOFC batteries, oxygen is used to oxidise divalent vanadium ions to trivalent ions in a bid to achieve potentially higher energy densities and eliminate temperature stability problems associated with the energy storage medium [12,14–18]. In recent years, this energy converter has been developed more and more, with regenerative concepts and concepts such as the vanadium/air redox flow battery (VARFB) also being investigated [19–21]. Reversing the reactions in a cell is beneficial as it means that the same cell area is used for both reactions. This could potentially save costs as, from an optimistic perspective, the amount of cell area and process technology required could be reduced. For this to happen, however, the conversion and reconversion reactions have to take place as quickly as they do in a system that uses two separate cells for each reaction (fuel cells + electrolysers). Using separate cells also has its benefits as each cell can be optimised for the reaction it performs. And if the partial reactions take place at different speeds, this could also reduce cell area relative to the VARFB concept as the charging and discharging reactions could take place much faster than in a reversible system. With the exception of Hosseiny et al. [19] and Grosse Austing et al. [20,21], V^{2+} solutions have been produced in vanadium redox flow batteries via the electrolysis of vanadium

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solutions. In these cases, however, a closed cycle cannot be formed and vanadium(V) solutions are generated as a waste product. To charge a VARFB and/or operate a VOFC as an energy storage system, the discharge reactions have to be reversed with as few side reactions as possible. This process involves reducing trivalent vanadium ions to divalent vanadium ions through the application of electrical energy. The cathodic water generated during the discharge is used as the reductant. The water itself is oxidised to oxygen to keep the cycle between the charge and discharge processes as short and efficient as possible:

$$\text{Anode}: \quad 2H_2O \leftrightarrow O_2 + 4H^+ + 4e^- \quad \varphi_A^0 = +1.23V$$

$$\text{Cathode}: \quad V^{3+} + e^- \leftrightarrow V^{2+} \quad \varphi_C^0 = -0.255V$$

$$\text{Cell}: \quad 4V^{3+} + 2H_2O \leftrightarrow O_2 + 4V^{2+} + 4H^+ \quad \varphi_Z = 1.49V$$

Platinum is often used as a catalyst for the oxygen reduction reaction (ORR). To keep the amounts, and therefore the cost, of this expensive precious metal catalyst low and to ensure the optimum configuration of the triple phase boundary layer, the cathodes for the ORR are complicated structures comprising many different components and materials [22]. Carbon is usually used to bond platinum to a membrane as it forms layers of interconnected conductive and porous bridges. The gas diffusion layer (GDL) also comprises a carbon-based structure [23]. In principle, the oxygen evolution reaction (OER) can be carried out on platinum electrodes. However, due to the presence of the other carbon-based materials in the half-cell, it is not possible to achieve potentials much over 1.3 V vs. NHE. This is because carbon would only offer a very narrow potential window for OER with Pt/C due to the formation of surface oxides, intercalations and, finally, oxidation via CO to CO_2 [24]. Carbon-based anodes are therefore not stable enough for long-term use in the OER even though it has been demonstrated that a VARFB with an Ir-modified graphite felt anode is capable of performing four charge and discharge cycles [20]. A proton exchange membrane water electrolyser (PEMWE) can be operated with alkaline and acid electrolytes, whereby different electrodes and catalysts are used in each case with even non-precious catalysts [25–27]. To reverse the reactions of a VOFC, electrolysis has to take place in an acid environment to ensure the requisite stability of the vanadium solutions. As a result, iridium oxide can be used as the catalyst and titanium that has been passivated with layers of oxide yet is still capable of conducting electricity can be used as support [25,26]. Typical PEMWEs operate at temperatures of between 50 and 80 °C and achieve current densities of up to 2 A/cm^2 [28,29]. Using platinum as a catalyst for the cathodic hydrogen evolution reaction (HER) causes the anode to polarise much more with IrO_2 than the cathode and this is the primary cause of the efficiency losses [26,27]. In PEMWEs, the anodes and cathodes can, theoretically, be polarised indefinitely as water is the solvent that needs to be broken down. However, for reversing the reactions of a VOFC or VARFB, V^{3+} has to be reduced to V^{2+}. This is a reaction with −0.255 V of standard potential and is therefore only around 150 mV more positive than HER with carbon. As a result, in contrast to PEMWEs, the polarisation of the cathode should be kept below the HER limit to prevent side reactions. This paper investigates separate electrolysis as a vanadium PEMWE (V-PEMWE) in order to draw conclusions about the viability and performance of this kind of system, which, ultimately forms the basis for an energy storage concept based on a VOFC and electrolyser. In addition to this, a vanadium water electrolyser could also be used as an electrolyte regeneration unit for vanadium solutions used in vanadium redox flow batteries that have been oxidised by atmospheric oxygen.

2. Experimental

As shown in Fig. 1, an electrolysis cell is operated with different vanadium solutions in order to investigate the different properties of a vanadium/water electrolyser (V-PEMWE). The cell comprised two half-cells separated by a commercial catalyst coated membrane (CCM) coated on one side (fumea®, 2.5 mg/cm^2 iridium, Fumatech GmbH, Germany). The cell had a geometrically active area of 40 cm^2. The cathodic half-cell consisted of a 3-mm thick PVC-based flow frame into which a thermally treated graphite felt (1 h, 400 °C, GFA-6, SGL carbon, Germany) was placed. The half-cell was enclosed with a graphite composite plate (FU 4369, Schunk-Kohlenstofftechnik GmbH, Germany) A commercial vanadium electrolyte solution (GFE-Metalle Nuremberg, Germany) was circulated through the cathodic half-cell using a membrane pump. This commercial electrolyte solution was an equal mixture of V(III) and V(IV) and consisted of 0.4 M $V_2(SO_4)_3$ and 0.8 M $VOSO_4$ in 2 M H_2SO_4 and 0.05 M H_3PO_4. This equal mixture was referred to as $V^{3.5+}$-solution in the following text. The anodic half-cell comprised the catalyst layer of the CCM, a titanium gas diffusion coating (MAGNETO Special Anodes B.V., Netherlands) and a titanium plate with four parallel and meandering flow channels. No medium was actively passed through the anode. However, the inlet and outlet lines were left open. The titanium plate on the anode and a copper plate behind the graphite plate on the cathode were used as current collectors. The cell was held together by two metallic end plates and the components were sealed using several EPDM sheets cut to size. The storage tank for the vanadium solution contained a mercury(I) chloride reference electrode and a glassy carbon electrode. This made it possible to not only measure cell voltage φ_Z but also the cathode potential φ_C and the redox potential $\varphi_{N,C}$ of the vanadium solution and the cathode impedances. All measurements were made at room temperature using a potentiostat (Reference 3000, Gamry Instruments, USA).

The measurements were made in the following sequence, starting with a $V^{3.5+}$ solution:

1. Open-circuit voltage and potentials ($V^{3.5+}$) (OCV &OCP)
2. Polarisation curves ($V^{3.5+}$)
3. Electrochemical impedance spectroscopy (EIS) ($V^{3.5+}$)
4. Electrolysis of $V^{3.5+}$ to V^{3+}
5. Open-circuit voltage and potentials (V^{3+})
6. Polarisation curves (V^{3+})

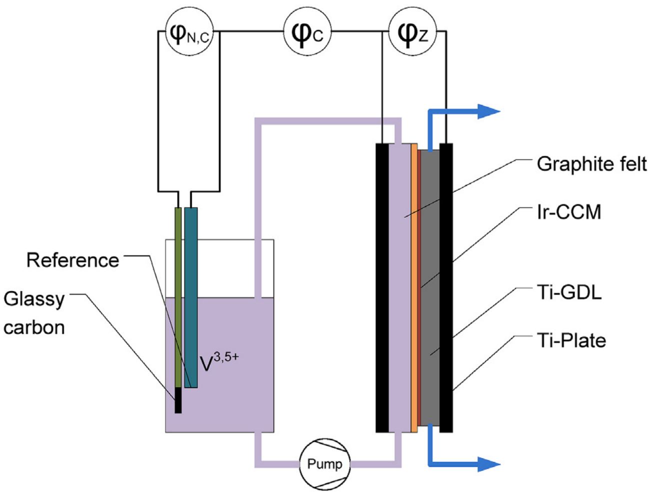

Fig. 1. Scheme of the test set-up for investigating a V-PEMWE.