



Study of the long-term operation of a vanadium/oxygen fuel cell



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HIGHLIGHTS

- Long-term operation of a vanadium/oxygen fuel cell over a period of over 676 h.
- Increased performance of the anode behaviour during the operation.
- Localization of aging causes at cathode reaction and cell compartments.

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ABSTRACT

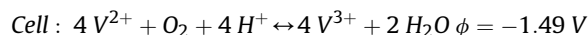
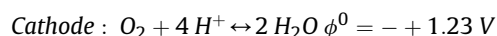
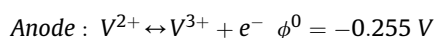
A vanadium/oxygen fuel cell (VOFC) with a geometrically active area of 51 cm² and two membranes was discontinuously operated over a period of over 676 h with 47 successive tests at room temperature with a current density of 19.6 mA/cm² in order to investigate signs of ageing. As well as measuring cell voltages, the test setup was also used to measure anode and redox potentials as well as cell and half-cell impedances. The performance data of the VOFC fluctuated widely over the course of the test period, due to different V²⁺ concentrations and instabilities of the starting solutions on the one hand and complex changes in cathode conditions on the other. The desired behaviour of the anode reactions was achieved primarily through improved methods for producing the V²⁺ solutions, and remained stable at the end of the experiments. The kinetics of the cathode reactions were temporarily increased by purging with 2 M H₂SO₄, however their performance decreased over time. The VOFC had symptoms of ageing by complex and overlaid changes in the cathode's triple phase boundary layer and in the special conditions between the two electrodes and membranes.

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1. Introduction

The growth in the use of renewable energy sources in power grids is accompanied by a rise in the demand for energy storage to bridge supply shortfalls [1,2]. Stationary electrochemical energy storages are particularly vital as they enable energy to be stored locally [3]. Important examples are lead/acid batteries, lithium/ion batteries and fuel cells/electrolysers [4]. There is also a huge number of battery chemistries suitable for niche applications or which are currently the object of research or commercialisation efforts [5–7]. The most important factor for comparisons and for the commercial success of stationary storage systems is not their investment costs but the levelized cost of energy (LCOE), a formula used to measure storage costs over a storage system's lifetime [8].

Energy storages with an inexpensive energy storage material therefore have a potentially low LCOE if the storage times are several hours or more. For average storage times therefore it is advisable to separate energy and power as is possible with fuel cells and redox flow batteries [9,10]. One example of this technology is the vanadium/oxygen fuel cell (VOFC) or vanadium/air redox flow battery (VARFB) that is based on conversions of oxygen and divalent vanadium.



The oxidation of V²⁺ which takes place in acidic media is coupled with an oxygen reduction reaction (ORR) to achieve a

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theoretical open-circuit voltage which at 1.49 V is rather higher than with conventional H_2/O_2 proton exchange membrane fuel cells (PEMFC). This has two particular advantages compared with vanadium redox flow batteries (VRFB). By replacing the redox pair $\text{VO}^{2+}/\text{VO}_2^+$ with an oxygen reduction reaction a condensation reaction of the pentavalent vanadium is prevented and the temperature range can be extended over 40 °C to increase the kinetics and save auxiliary components. The theoretical energy density can be increased significantly by higher solubilities of V^{2+} and V^{3+} and the use of a single electrolyte. This system was first described by Kaneko et al. in his patent in 1992 [11]. In 2010 we reported on a comparison of a vanadium/oxygen fuel cell with a VRFB in which the VOFC delivered similar performance values [12]. In 2011 Hosseiny et al. reported on the construction and testing of a vanadium/air redox flow battery (VARFB), i.e. a reversible VOFC [13]. However different membrane electrode assemblies (MEA) were used for charging and discharging with the same Pt/Ir catalyst, so actually a fuel cell and an electrolyser were investigated separately. Charging and discharging took place galvanostatically at 2.4 mA/cm² at different temperatures. Up to 46% energy efficiency at 80 °C was achieved, although only one cycle each was shown. Menictas et al. reported on investigations and developments of so far the only VOFC stack with 5 cells [14]. They found signs of delamination of the catalyst layer on the MEA which had swollen during operation, resulting in performance losses. Without quoting any data, an optimized stack should have completed over 120 h of operation with no loss of performance. We also found significant performance losses over just a few hours with a pre-swollen catalyst coated membrane (CCM) of NAFION and Pt/C, and were able to attribute this behaviour to the evolution of hydrogen on the cathode caused by diffused V^{2+} ions [15]. To overcome this problem we developed a cell design with two membranes [17,18]. In 2015 grosse Austing et al. showed a VARFB based on Pt/C and IrO_2 with a two-layered cathode with which they demonstrated 4 charge and discharge cycles at 20 mA/cm² with decreasing voltage efficiency [16]. Gutsche et al. investigated the influence of vanadium on the ORR, OER and on the catalyst degradation of Pt/C catalysts with 0.1 M VOSO_4 in 2 M H_2SO_4 by means of cyclic voltammetry and electrochemical quartz crystal microbalance (EQCM) [20]. Their investigations revealed no influence of vanadium at this concentration on the activity and ageing of the ORR.

To date however there have been no meaningful or repeatable investigations of a VOFC system over long-term operation but just for a few cycles or hours. To achieve a system that is efficient in

the long term it is important to know what the problems are which arise and which processes they can be attributed to. In this context it was particularly important to ascertain which components start to age first in such a system so as to be able to target further investigations. The aim of this work was to be able to operate and investigate a cell over the longest possible period of time especially with the described problems of MEA delamination [14], the migration of divalent vanadium to the cathode [18,16] and the influence of vanadium on the cathode. As part of the present investigations therefore a VOFC based on two membranes and with a geometrically active area of 51 cm² was built and discharged with 1.6 M V^{2+} solutions and atmospheric oxygen at room temperature. In addition to the cell voltages, a reference electrode was used to measure redox potentials of the electrolyte solutions and anode potentials. A dynamic hydrogen electrode (DHE) in the cathode half-cell allowed the direct measurement of the cathode impedance spectra in addition to those of the cell and the anode. Open-circuit voltages and potentials, polarisation curves and impedances were measured before each discharge operation step.

2. Experimental

2.1. Cell

The investigations were carried out with a modified cell design with a geometrically active area of 51 cm² as shown in Fig. 1a. The cell consisted of two membranes (NAFION[®] 115, Dupont, USA) and was intended to prevent the migration of divalent vanadium to the cathode [17,18]. Basically the cell consisted of a flow-through anode and a flow-by cathode. The anodic half-cell consisted of a flow frame with an embedded carbon composite plate (FU 4396, Schunk Kohlenstofftechnik GmbH, Germany) and an inserted graphite felt treated thermally at 400 °C for one hour (GFA5, SGL-Carbon GmbH, Germany). Reference electrodes could be incorporated through holes through the end, isolation plate and composite plates, but were not used during these experiments. The flow frame had inlets and outlets to allow a continuous flow of divalent vanadium solution through the graphite felt. The half-cell was separated by a membrane (NAFION[®] 115, Dupont, USA). This was followed by a cavity structure with a thickness of 20 mm, also separated by a NAFION[®] membrane. The cavity structure had two bores for inserting reference or working electrodes to measure the redox potential in the cavity, for example. The cavity structure had inlets and outlets for the continuous flow of electrolyte solution. No

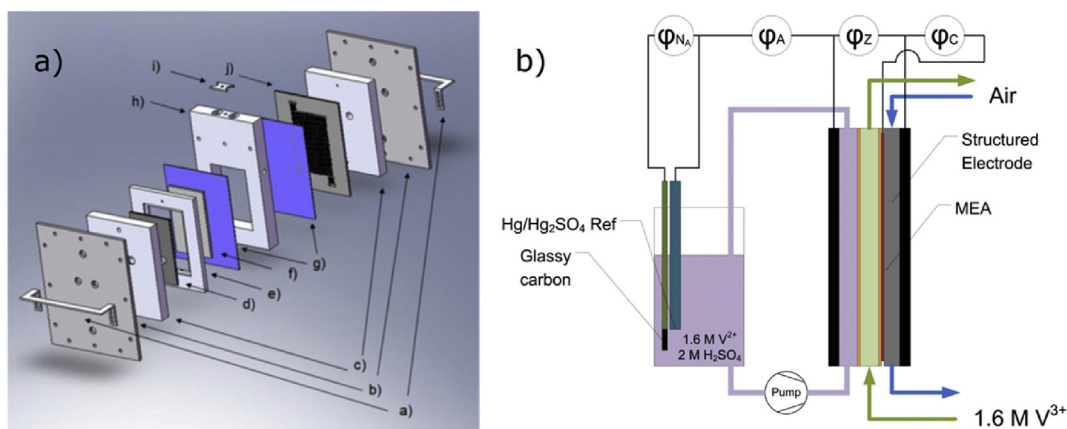


Fig. 1. a) Schematic cell layout of a 51 cm² VOFC with two membranes (a – reference electrode holder, b – end plates, c – isolation plates, d – carbon composite plate, e – flow frame, f – graphite felt, g – membranes, h – gap frame, i – electrode holder, j – carbon composite plate with meander structure); b) Schematic setup of the long-term test.

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