



Development and characterization of a 280 cm² vanadium/oxygen fuel cell



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HIGHLIGHTS

- A vanadium/oxygen fuel cell with an active area of 280 cm² has been developed and tested.
- The cell uses 2 membranes to avoid side reactions on the platinum ORR catalyst.
- The cell performance has been compared to a 50 cm² design and had nearly similar values.
- In both cells, the performance was limited by slow oxygen reduction rate at room temperature.

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ABSTRACT

A vanadium/oxygen fuel cell with an active area of 280 cm² has been developed. The cell consisted of two membranes with two half-cells and an intermediate chamber. The maximum achieved power density was 23 mW cm⁻² at 0.56 V with lambda air = 3 and a 1.6 M V²⁺ solution at room temperature. The average discharge power density was 19.6 mW cm⁻² at a constant current density of 40 mA cm⁻² with an average voltage efficiency of 33%. The fuel based energy density was 18.2% of the theoretical value with 11.8 Wh L⁻¹. In comparison with a similarly constructed 50 cm² cell, both achieved similar performance levels. An analysis using the half-cell potential profiles and by means of impedance spectroscopy revealed that, as for the 50 cm² cell, the low rate of oxygen reduction reaction significantly affected the performance of the cell. Thus gives potential for the optimization of the cathode reaction and a reduction in the ohmic resistances potential for higher power densities.

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1. Introduction

With a reduction in the production of crude oil with at the same time increasing demand, massive price increases are expected [1]. Motorized transport is almost exclusively tied directly or indirectly to the cheap availability of crude oil or natural gas. To have in the future low-cost alternatives available, currently intense research on alternative concepts is made. The most promising technology is the electro-mechanical propulsion of vehicles by the use of electro-chemical energy converters and -storage. Currently the biggest hurdle for broad market introduction is the availability of inexpensive electrochemical storage systems. In addition, there are other technology-related issues such as durability, reliability, recoverability, range (capacity), temperature behavior, etc. [2]. Batteries such as Lithium-Ion Batteries (LIB) do not have sufficiently high energy densities for longer distances with an acceptable

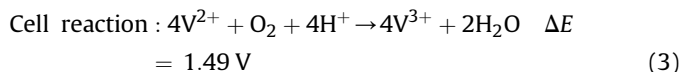
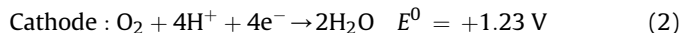
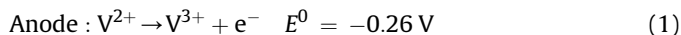
amount of time, because a lot of the time must be used for recharging. Fast charge capable systems such as of spinel type Li₄Ti₅O₁₂ lithium titanate based LIBs have lower energy densities [3–5], require high, also fluctuating performance in an electrical grid with an increasing proportion of fluctuating energy sources. In contrast, fuel cells offer high energy densities [6] and acceptable lifetime. However, the use of hydrogen as an energy carrier requires complex, loss-prone and expensive handling, but the electro-chemical production process is well established by the electrolysis of water, methods such as the photocatalytic water splitting are in development [7]. An alternative could be systems in which electrical energy is stored by an energy converter in dissolved redox couples like redox flow batteries are [8,9]. The energy density of 20–80 Wh L⁻¹, based on the energy carrier fluid, is too low for mobile applications, but in general electrical regenerability and fast charge by changing the energy carrier fluids are given.

An often as vanadium redox flow battery or vanadium air oxygen fuel cell (VOFC) designated system uses dissolved vanadium ions as an energy source and oxygen as oxidant [10].

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The reaction equations are as follows:



Here, the theoretical maximum energy density increased from 30 to 60 Wh L⁻¹ compared to the vanadium redox flow battery (VRFB) by a factor of two, when using the same 1.6 M vanadium sulphate solution. Since the energy density in a VRFB is limited by the solubility of pentavalent VO₂⁺ and the time-, concentration- and temperature-dependent formation of heteropolyacids by condensation, higher concentrations and thus energy densities in VOFCs could be realized with divalent and trivalent vanadium sulfate solutions. In addition to automotive applications also stationary applications are conceivable in which higher energy densities are desirable. In previous work different components and modes of operation with single cells and a 5-cell stack was studied [11]. A major challenge was the delamination of the catalyst layer of the catalyst coated membrane (CCM) by swelling, which could be reduced, however, so a 5-cell stack could be operated over a period of about 120 h. Hosseiny et al. reported a vanadium air redox flow battery (VARFB) called VOFC in which they exchanged the membrane electrode assembly (MEA) between charging and discharging with one having a different catalyst [12]. For discharge a platinum/carbon based (MEA) was used, for charging a titanium/iridium based was used. Our group reported an experimental comparison of a VOFC with a VRFB [13]. Like Menictas et al., we found a strong power loss during discharge of the cell and we attributed this to hydrogen evolution at the Pt-based catalyst by electro-migrated divalent vanadium, whereupon we developed a cell with two membranes to avoid this problem [14,15]. In this work we were interested in the upscaling of the cell and optimization of cell components to be able to build efficient cell stacks. Furthermore, we investigated operating parameters of the system, limitations and optimization possibilities. For more information about the causes of limitations, the values were compared with a 50 cm² cell, where in addition cathode-, anode- and redox potentials and -impedances were measured. We also wanted to provide more comparable data, for example energy- and power densities, impedances and potentials of cells and half-cells for further studies and developments.

2. Experimental

As shown in Fig. 1, a stackable design has been developed and a single cell was constructed with a geometric active area of 280 cm². The cell consisted of two half-cells separated by two membranes. Between the two membranes was a chamber in which a separate liquid could flow through. The anodic half-cell consisted of a PVC flow frame (d), a graphite foil (Sigracet TF6, SGL Carbon GmbH, Germany) and several layers of graphite felts (GFA5, SGL Carbon GmbH, Germany). The separation of the anodic half-cell was made by a NAFION[®] 115 membrane (DuPont, USA). The cathode half-cell consisted of a flow-through frame (h), a graphite foil, graphite felt (Sigracet TF6, GFA5, SGL Carbon GmbH, Germany), a gas diffusion layer (X0070, Freudenberg FCCT KG, Germany) and a catalyst coated membrane (CCM CC 0.6–0.8 mg cm⁻² Pt on NAFION[®] 212, 20 wt% NAFION[®] ionomer in catalyst layer, Quintech GmbH, Germany). Between the two half-cells was a cavity formed by a flow frame (f), which was separated by the two membranes of anodic

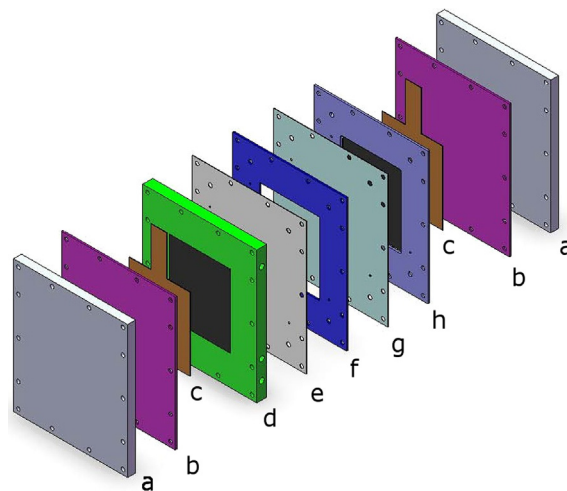
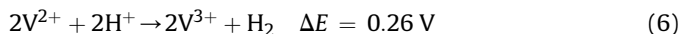


Fig. 1. 280 cm² VOFC components (a – end plate, b – isolation plate, c – current collector, d – anodic flow frame, e – membrane, f – gap flow frame, g – catalyst coated membrane, h – cathodic flow frame).

and cathodic half-cells. As a spacer, a graphite felt was placed in the cavity. The purpose of this cavity was to avoid the diffusion of divalent vanadium (V²⁺) ions to the Pt-catalyst. V²⁺ solutions with their negative redox potential are not kinetically hindered on platinum electrodes and are rapidly oxidized by reduction of protons, which leads to the evolution of hydrogen and probably the delamination of the catalyst layer by the following reactions:



Therefore the cavity was rinsed by a pump with 2 M sulfuric acid in cycle. The sulfuric acid was gassed externally with air to maintain the redox potential of the solution above a value of 0.1 V vs. NHE in order to oxidize any V²⁺ entering into V³⁺ to prevent the evolution of hydrogen gas at the cathode. Consequently over time a constant concentration of V³⁺ should be reached in the cavity cycle with V³⁺ leaking to the cathode without causing hydrogen evolution.

Air at atmospheric pressure was used as the oxidant in the cathodic half-cell which was regulated by a mass flow controller. The anode cycle was filled with a defined amount of 1.6 M V²⁺ solution which was circulated by a pump through the graphite felts. The solution was prepared electrolytically in an electrolytic cell. A solution of 0.8 M VOSO₄, 0.4 M V₂(SO₄)₃, 2 M H₂SO₄ and 0.05 M H₃PO₄ (GFE-Metalle GmbH, Nürnberg, Germany) was electrolyzed until the catholyte redox potential was –1.1 V vs Hg/Hg₂SO₄. A cell with a geometric active area of 50 cm² was used, with a similar structure to the 280 cm² cell with a dynamic hydrogen electrode (DHE) on the cathode side of the CCM [16]. The DHE was employed during electrochemical impedance measurements. For these measurements a reference potential is required which is stable for the duration of the measurements of several minutes. To achieve the desired stability the DHE was covered with adhesive tape to prevent hydrogen removal and was operated at a current of 30 μA. Thus the potential of the DHE should be constant at about 0 V vs. RHE over the required period of time. Instead of graphite foils, graphite composite plates with thicknesses of 3 mm were used (FU 4396, Schunk Carbon GmbH, Germany). The CCM had a platinum loading of 1 mg cm⁻² and 20 wt% NAFION[®] ionomer in the catalyst

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