J Appl Electrochem (2011) 41:1223–1232
DOI 10.1007/s10800-011-0342-8

ORIGINAL PAPER

Performance of vanadium-oxygen redox fuel cell

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Received: 6 December 2010 / Accepted: 26 July 2011 / Published online: 27 September 2011

Abstract A promising approach to improving the energy density of the all-vanadium redox flow battery while also saving on raw materials costs, is to eliminate the positive half-cell electrolyte and replace it with an air electrode to produce a hybrid vanadium–oxygen redox fuel cell (VOFC). This concept was initially proposed by Kaneko et al. in 1992 and first evaluated at the University of New South Wales by Menictas and Skyllas-Kazacos in 1997. In this project the performance of the VOFC over a range of temperatures and using different types of membranes and air electrode assemblies was evaluated. Despite early problems with the membrane electrode assemblies that saw separation of the membrane due to swelling and expansion during hydration, with improved fabrication techniques, this problem was minimized and it was possible to operate a 5-cell VOFC system for a total of over 100 h without any deterioration in its performance.

Keywords All-vanadium redox flow battery · Redox fuel cell · Electric vehicles · Energy storage

1 Introduction

The vanadium redox battery (VRB) system was pioneered by Skyllas-Kazacos et al. at the University of New South Wales and has been under development in the School of Chemical Engineering at UNSW since 1984 [1–21]. The early part of the research and development work at UNSW concentrated on the redox chemistry of the vanadium couples [3, 4], the selection, characterization and activation of electrode [5–8] and membrane materials [9–13], development of conducting plastic bipolar electrode substrates [14], electrolyte characterization, optimization, stabilization and production [15–18], stack design, control system development and field trials in a Thai solar house and electric golf cart [19, 20]. Major progress has been made in recent years and the VRB system is now ready for commercialisation in load levelling and small-scale to large-scale renewable energy storage applications [21–25].

The VRB system has many advantages over conventional batteries, but one of its most attractive features for electric vehicle applications, is its ability to be both electrically and mechanically recharged in situ. Since the VRB system employs liquid electrolytes, instant recharge is possible by simply exchanging the discharged electrolytes with recharged solutions. This "refueling" could be done at special refueling stations where the discharged solutions could then be regenerated using off-peak electricity or excess wind or solar energy.

While this feature makes the VRB system very attractive for electric vehicle applications, the present energy density of the Generation 1 all-vanadium redox battery employing vanadium redox couples in sulphuric acid supporting electrolyte would limit its use mainly to buses, vans and off-road vehicles. While the present energy density of around 20 Wh kg^{-1} is adequate for stationary applications, this needs to be increased considerably before it begins to be in serious contention for wider electric vehicle applications.

Two parallel areas of research were undertaken at UNSW to increase the energy density of the vanadium battery. The first approach was to identify an alternative half-cell electrolyte with a higher vanadium salt solubility. This study led to the successful development of the

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Generation 2 vanadium bromide redox cell that uses a vanadium bromide solution in both half-cells [26, 27]. The significantly higher solubility of vanadium bromide species will allow the energy density to be potentially doubled and further work is currently underway to optimize low cost bromine complexing agents to bind the bromine produced at the positive electrode to form a stable organic oil that prevents the formation of any vapours [21].

A second approach that can also save considerable costs in the vanadium raw material used in the vanadium flow battery is to eliminate one of the half-cell electrolytes by replacing the positive half-cell with an air electrode to produce a hybrid vanadium-oxygen redox fuel cell. As the VRB system uses vanadium electrolytes in both the negative and positive half-cells, eliminating or minimising one of the electrolytes will effectively double the energy density of the system.

The vanadium–oxygen redox fuel cell (VOFC) concept was initially proposed by Kaneko et al. in 1992 [28] and first evaluated at UNSW by Menictas and Skyllas-Kazacos in 1997 [29]. With renewed interest in electric vehicles however, the concept has recently received further attention with a range of a reports emerging from the Fraunhofer Institute [30] and Twente University in the Netherlands [31].

This project was therefore undertaken in order to evaluate the performance of the VOFC over a range of temperatures and using different types of membranes and air electrode assemblies to establish the feasibility of a VOFC with energy density over 40 Wh $kg^{-1.}$

2 V/O_2 redox fuel cell concept

In the standard all-vanadium redox battery (VRB) system the V(II)/V(III) redox couple is utilised in the negative half-cell while the V(IV)/V(V) redox couple provides the positive half-cell reaction as given by:

Negative half-cell reaction

$$V^{3+} + e^- \Leftrightarrow V^{2+}, \quad E^\circ = -0.26\,V \tag{1}$$

Positive half-cell reaction

$$VO_2^+ + 2H^+ + e^- \Leftrightarrow VO^{2+} + H_2O, \quad E^\circ = 1.00\,V \tag{2}$$

In the vanadium–oxygen redox fuel cell (VOFC) system, the negative half-cell reaction remains unchanged. At the positive electrode however, the V(IV)/V(V) redox reaction is replaced by the oxygen reduction reaction:

Oxygen reduction reaction:

$$O_2 + 2H^+ + 2e^- \Leftrightarrow H_2O, \quad E^\circ = 1.23\,V \tag{3}$$

From Eqs. 2 and 3 above, it can be seen that the standard cell potential for the VOFC is higher than for the VRB, however, given that the overpotential for oxygen reduction is relatively high, actual cell voltages may still be lower than for the VRB, and this would depend on the catalytic activity of the oxygen diffusion electrode used in the cell.

The purpose of the present study was to initially confirm the viability of the VOFC system using off-the-shelf oxygen diffusion electrodes and establish the important parameters that need to be addressed for the development of a practical system.

3 Experimental

3.1 Materials and cell design

The VOFC system utilised ELAT gas diffusion electrodes manufactured and supplied by E-Tek Inc. Pty. Ltd. (USA). The gas diffusion electrodes used had dimensions 20 cm × 20 cm and comprised a plain weave carbon cloth support of 116 g m^{-2} and thickness of 0.36 mm. Catalyst loadings on the samples provided were 0.4 and 1.0 mg Pt cm^{-2}.

Two different membranes were evaluated for use in the VOFC system. These were Nafion 112 and Nafion 117. The membrane was first bonded to the catalysed surface of the gas diffusion electrode by hot pressing to produce a membrane electrode assembly (MEA).

The main cell components of the VOFC stack assembly are illustrated in Fig. 1. A stainless steel current collector was used behind the gas diffusion electrode and graphite felt was incorporated between the gas diffusion electrode and the stainless steel current collector to allow oxygen to be fed to the back of the electrode while still allowing current collection. The negative half-cell comprised a 1.5 mm PVC flow-frame with inlet and outlet channels for the negative electrolyte. A 1 mm neoprene rubber gasket was placed on each side of the flow-frame to provide a total cavity thickness of 3.5 mm into which was placed a piece of 5 mm thick graphite felt as the porous flow-through electrode (SGL Carbon, Germany). Unless otherwise stated, the negative electrolyte used in single cell tests comprised 50 mL of 1.8 M V(II) in 5 M H_2SO_4. This was prepared by reducing a V(IV)/V(III) solution obtained by suspended powder electrolysis of V_2O_5 powder. It should be mentioned that the choice of this electrolyte composition was arbitrary and given that the redox fuel cell design eliminates the positive electrolyte with its accompanying V(V) thermal precipitation issues, considerable optimization of the negative half-cell electrolyte composition is possible as part of any future work.

In early experiments, the gas feed to the positive half-cell was air at atmospheric pressure. In subsequent experiments oxygen gas was fed through the positive half-cell

Fig. 1 Cell components for VOFC assembly

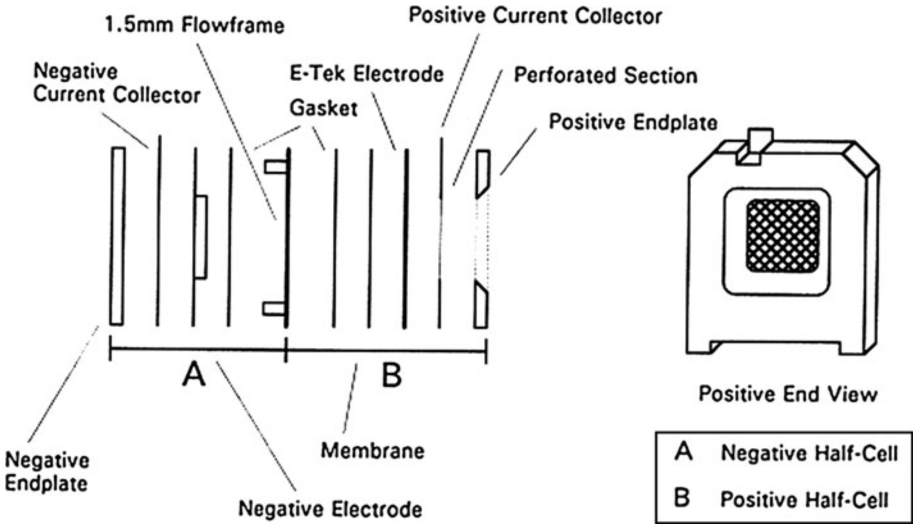
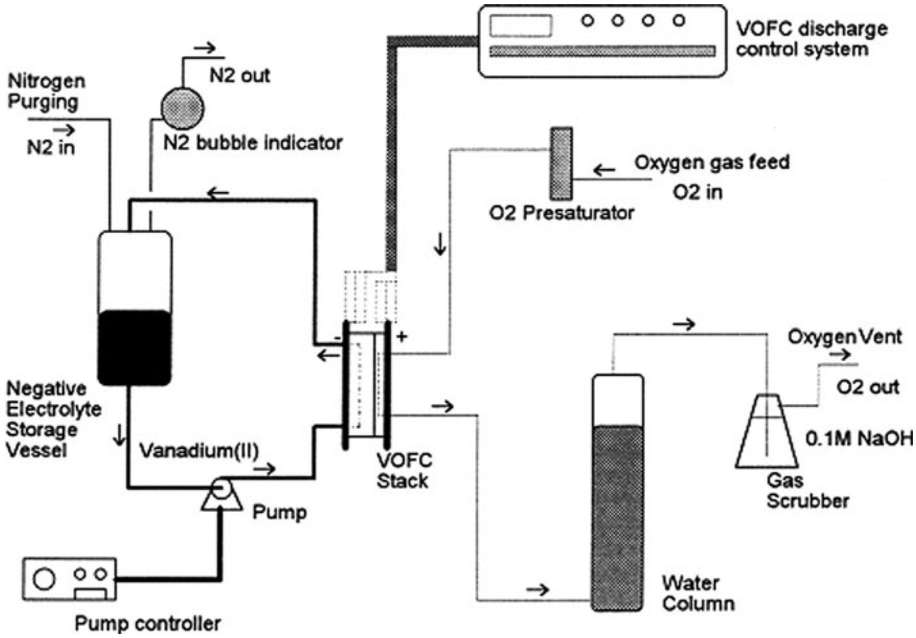


Fig. 2 Layout of the VOFC laboratory system



and a water column was used to provide O_2 back pressure in the system so as to improve mass transport of oxygen to the gas diffusion electrode. The layout of the VOFC apparatus is illustrated in Fig. 2. Unless otherwise stated, the same stack design, membrane and electrodes were used in each of the experiments detailed below.

3.2 5-cell VOFC stack assembly

A 5-cell VOFC stack assembly was also designed and fabricated to evaluate possible bipolar electrode configurations. A schematic representation of the 5-cell stack is presented in Fig. 3. The glassy carbon electrode in cell 1 was placed against the negative copper current collector. Section A in cell 1 represents the negative half-cell, while Section B represents the oxygen half-cell. To minimise the contact resistance the glassy carbon electrode in cell 1 only, was copper coated on one side using vapour deposition. The negative half-cell felt and the felt used to provide a conductive pathway from the back of the gas diffusion electrode to the glassy carbon electrode of the adjacent cell was a combination of a piece of 5 mm and a piece of 2 mm graphite felts (SGL Carbon). The conductive pathway also allowed the feeding of oxygen gas to the back of the gas diffusion electrode as illustrated in Fig. 3.

The dimensions of the 5 gas diffusion electrodes were 6.5 cm × 6.5 cm and these were Nafion coated on the catalysed side using the method detailed above. Once the stack assembly was completed the electrolyte and gas distribution manifolds were assembled and connected to the battery stack.

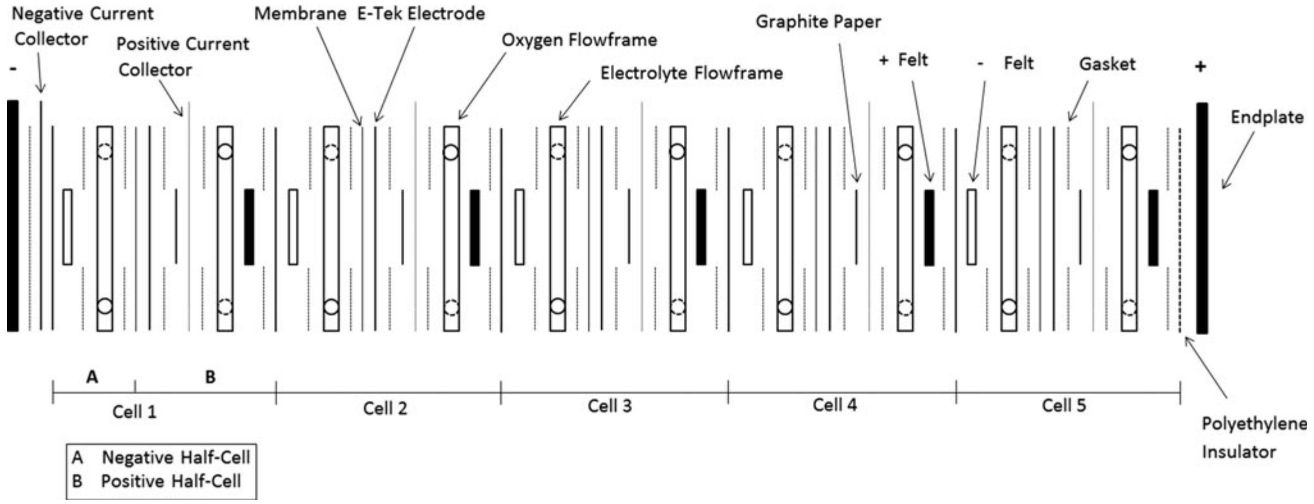


Fig. 3 Schematic of 5-cell stack

4 Results and discussion

4.1 VOFC employing Nafion 112 membrane

Initial trials were carried out using an air gas feed to the positive electrode at atmospheric pressure and room temperature (18.5 °C). A commercially available gas diffusion electrode supplied by E-Tek Inc. (ELAT Type) with catalyst loading of 0.4 mg Pt cm^{-2} was coated with Nafion solution giving a Nafion loading of 0.49 mg cm^{-2}. A sheet of Nafion 112 was then bonded onto the Nafion coated side of the gas diffusion electrode to produce a MEA that was then incorporated into the VOFC and tested at various discharge currents.

The OCV was measured a few minutes after the V(II) solution was fed through the negative half-cell of the VOFC and a value of 1.33 V was recorded. The operating cell voltages shown in Table 1 were observed at various current densities after the system was allowed to stabilise for 5-10 min at each current density. The cell voltage values given in Table 1 were plotted against current density and the polarization curve obtained for the cell operating at room temperature with the Nafion 112 membrane gave a regression line corresponding to $y = -0.11x + 0.8775$. From the slope of this plot, a cell resistance of 11.1 ohms cm^2 was calculated. This high cell resistance is a combination of ohmic and polarization losses and the high value is likely to be associated with the high activation energy that is expected for the oxygen reduction reaction at room temperature.

Continuing the above trial, the operating temperature of the cell was then increased to 53 °C in an effort to reduce the activation overvoltage losses and improve the cell voltage. On discharging at 20.8 mA cm^{-2} the initial discharge voltage was 0.736 V. As summarised in Table 1, a discharge voltage of 0.725 V was recorded after 7 min, significantly higher than the corresponding value at ambient temperature.

The system temperature was then increased to 65 °C and the discharge current density reduced to 10.1 mA cm^{-2}. After 5 min the cell voltage leveled off at 0.820 V compared to 0.763 V obtained at ambient temperature. When the discharge current density was reduced to 5.4 mA cm^{-2} the operating voltage stabilised at 0.864 V compared to 0.842 V at ambient temperature. These results show a significant effect of temperature on the VOFC operating voltage as would be expected.

In a second experiment, an E-Tek (ELAT) gas diffusion electrode with the same catalyst loading of 0.4 mg Pt cm^{-2}, was coated with Nafion solution giving a Nafion loading

Table 1 Observed cell voltages at various current densities and temperatures for cell employing ELAT gas diffusion electrolyte with catalyst loading of 0.4 mg Pt cm^{-2} and Nafion 112 membrane

Current density (mA cm^{-2})	Cell voltage at room temp (V)	Cell voltage at 53 °C (V)	Cell voltage at 65 °C (V)
5.4	0.842	–	0.864
10.1	0.763	–	0.820
20.8	0.613	0.725	–
30.3	0.526	–	–
40.5	0.452	–	–

of 0.76 mg cm^{-2}. A sheet of Nafion 112 membrane was then bonded onto coated side of the E-Tek electrode to produce the MEA. This MEA was then tested in the VOFC under the same conditions as above except that a fresh V(II) solution was employed. In this case, the initial open circuit voltage was 1.410 V, showing that this solution was closer to 100% state-of-charge than the previous test solution that had undergone partial self-discharge due to air oxidation of the V(II) ions on standing.

The cell was discharged at 10 mA cm^{-2} and an initial discharge voltage of 0.96 V was obtained. On continuous discharge at 10 mA cm^{-2} the operating voltage dropped to 0.82 V after 30 min. The higher Nafion loading is expected to improve the contact between the membrane and the oxygen diffusion electrode, allowing enhanced diffusion of the current carrying hydrogen ions across the membrane and a corresponding lower ohmic voltage drop across the cell.

The discharge current density was reduced to 5 mA cm^{-2} and the operating voltage of the system was 0.91 V after 30 min continuous operation. After 1 h of continuous operation the OCV voltage was approximately 1.2 V.

Good performance was thus obtained with the MEA, however, when the VOFC was dismantled, areas of the membrane appeared to have lifted off the gas diffusion electrode. This delamination may have been caused by the expansion of the membrane since the membrane was bonded dry on to the electrode. When the MEA is operated in the cell the membrane becomes hydrated and expands. This phenomenon was also evident with the Nafion 117 membrane and is discussed further below.

4.2 VOFC employing Nafion 117 membrane

MEAs were constructed by bonding Nafion 117 membrane onto an E-Tek (ELAT) gas diffusion electrode that had first been coated with Nafion solution at two different loadings as described previously. The first MEA was produced by bonding the Nafion 117 membrane to an E-Tek gas diffusion electrode that had a catalyst loading of 0.4 mg Pt cm^{-2} that was previously coated with Nafion solution to a Nafion loading of 0.49 mg cm^{-2}. The MEA was then tested in a VOFC using oxygen gas feed at room temperature (19 °C) with a 2 ft water column back pressure.

The initial open circuit voltage was recorded as 1.402 V while the initial discharge voltage at 5 mA cm^{-2} was 1.06 V. At a discharge current density of 10 mA cm^{-2} the initial discharge voltage was 0.978 V stabilising to 0.965 V after 3 min. After a short time of operation the cell voltage was found to decay very quickly. The cell was dismantled and the MEA examined. It was discovered that the membrane had lifted off the gas diffusion electrode over approximately 50% of the MEA's active area. The reason for the MEA separation is believed to be due to the expansion of the membrane when it becomes hydrated in the VOFC system.

The expansion of Nafion 117 membrane was further investigated and it was found that after hydration of the membrane by boiling in distilled water for 30 min, then allowing it to cool, Nafion 117 membrane expanded by 18.5 and 8.2% in the x and y directions respectively, with a 21% increase in thickness. This expansion of Nafion when hydrated makes it extremely difficult to produce an MEA that retains its integrity during operation.

The operating voltage value above 1.00 V obtained here was significant however, since it demonstrated that acceptable operating voltages can be obtained for the VOFC system. A second experiment was therefore carried out with the same membrane, but this time the gas diffusion electrodes supplied by E-TEK Inc. had a platinum loading of 1.0 mg cm^{-2}, higher than the earlier samples containing 0.4 mg Pt cm^{-2}.

In these experiments the oxygen feed gas was pre-saturated in distilled water before entering the VOFC stack as illustrated in Fig. 2. The laboratory temperature was 24 °C with the open circuit voltage of the cell reading 1.35 V. The performance of this system was initially evaluated with oxygen gas feed at room temperature (24 °C) at a range of current densities between 5 and 40 mA cm^{-2}.

The results presented in Table 2 show that a cell voltage of 1.01 V can be sustained at a current density of 5.4 mA cm^{-2}. Experimentally, this voltage remained constant for approximately 2 h. As expected, the cell voltage decreases at high current densities, dropping to 0.52 V at 30 mA cm^{-2} and to less than 0.4 V at 40 mA cm^{-2}.

Effect of Pre-Heating Oxygen Feed Gas

Conventional fuel cells are generally operated with pre-humidified oxygen inlet gas at elevated temperature to improve the performance of the proton exchange membrane. A heater was thus placed under the oxygen pre-saturator and the water in the pre-saturator was brought to boil. At this point the line between the oxygen feed gas exit port on the VOFC and the inlet port of the water column was disconnected to allow the escape of trapped water. It was evident that some steam was exiting the oxygen outlet port on the VOFC.

The observed cell voltage values at different current densities with pre-heated oxygen feed gas, are also provided in Table 2 for different currents. At 30 mA cm^{-2} the voltage was 0.52 V before preheating of the feed gas, however, after preheating the voltage increased to 0.84 V and remained stable. After 10 min at 0.84 V the discharge current density was decreased from 30 to 20 mA cm^{-2}.

Table 2 Cell voltage versus current density for cell employing ELAT gas diffusion electrode with platinum loading of 1.0 mg cm^{-2} and Nafion 117 membrane

Current density (mA cm^{-2})	V(II) solution volume (mL)	Average discharge voltage during first 2 h no gas pre-heat (V)	Discharge voltage with oxygen pre-saturation and pre-heat (V)
5.4	50	1.01	1.08
20	35	0.75	0.92
30	45	0.52	0.84
40	45	<0.4	N/A

The cell voltage was now 0.92 V where previously at 20 mA cm^{-2} the cell voltage was 0.75 V. At 10 and 5 mA cm^{-2} the cell voltages obtained were 1.05 and 1.08 V respectively.

From these results, polarization plots were obtained and from the slopes of the lines of best fit, cell resistance values of 9.8 and 19.8 ohms cm^2 were calculated for the cell operated with and without oxygen gas pre-heating respectively. Comparing the unheated oxygen gas feed cell performance of this cell with the corresponding cell utilizing Nafion 112 membrane (thickness 50 μm), it is seen that the cell resistance is higher for the Nafion 117 membrane as expected. This is due to the greater thickness of Nafion 117 (170 μm) that gives rise to a higher ohmic resistance. With gas pre-heating however, the cell resistance of the Nafion 117 cell was reduced from 19.8 to 9.8 ohms cm^2. This dramatic decrease in cell resistance is due to the improved kinetics for the oxygen reduction reaction at the higher temperature that reduces the activation overvoltage for the reaction.

These results show that the pre-saturation and preheating of the feed gas has a significant impact on the cell resistance and should be further investigated for improving the operation of the VOFC system. The preheat temperature must be controlled however to prevent damage to the MEA.

4.3 Design, construction and testing of 5-cell VOFC stack

The Nafion 117 membrane and E-Tek electrodes with Pt loading of 1.0 mg cm^{-2} were used to fabricate and test a 5-cell stack for further testing of the VOFC. The completed 5-cell VOFC stack with the external distribution manifolds is shown in Fig. 4.

Once the 5-cell VOFC stack assembly was completed it was connected to a 2.5 L negative electrolyte storage vessel and an Iwaki MD-20 magnetic pump. The gas feed was industrial grade oxygen which was passed through a gas pre-saturator and pre-heater to heat up the feed gas to approximately 60 °C before passing it through the gas diffusion electrode. Since the vanadium (II) solution used as the negative half-cell electrolyte is readily oxidised by oxygen, the electrolyte storage tank was continuously purged with nitrogen for the duration of each experiment.

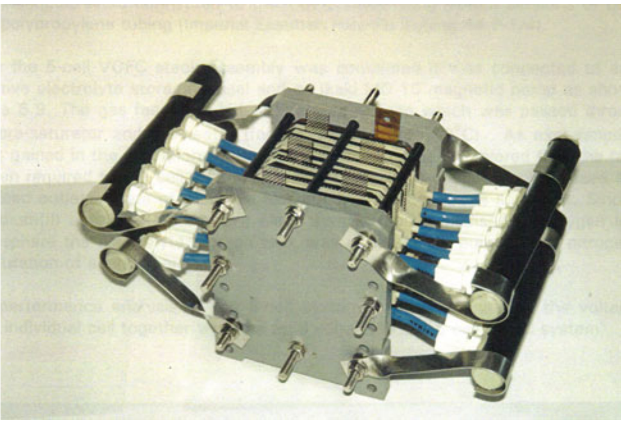


Fig. 4 Photograph of 5-cell stack

The performance analysis of the 5-cell system involved monitoring the voltage of each individual cell together with the total voltage of the 5-cell VOFC stack. The negative half-cell electrolyte (2.1 L) was fed through the negative half-cell while discharging the cell under a range of conditions.

The stack was first discharged at 6 mA cm^{-2} to determine the cell voltage distribution in the stack. A system characteristic often observed was that the initial discharge voltage of the system recovered slightly and tapered off to a flat discharge. This is illustrated in Fig. 5 that plots the cell discharge results obtained at the discharge current of 6 mA cm^{-2}. This suggests that some equilibration is occurring in the cell as a result of membrane or electrode conditioning during operation.

The results also show that the operating voltage of the 5-cell VOFC system leveled off at 5.2 V after 144 min of continuous discharge at 6 mA cm^{-2}. This corresponds to an average cell voltage of 1.04 V, however cell 4 peaked at 1.226 V after 122 min of operation. After 144 min of operation, four of the five cells had a discharge voltage over 1 V.

At t = 160 min the stack voltage was 5.12 V and the variation in VOFC stack voltage with increasing current

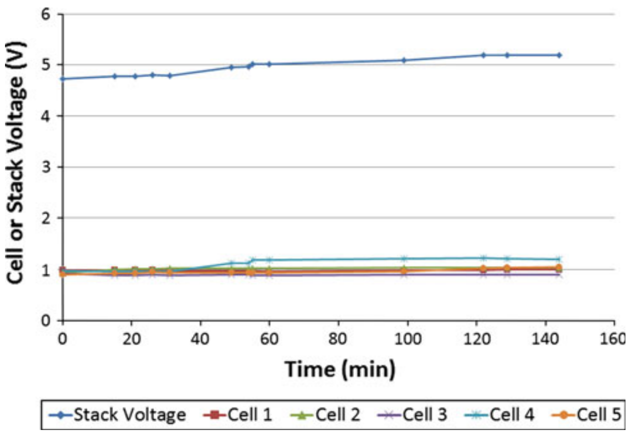


Fig. 5 Stack voltage and cell voltages at a constant discharge current density of 6 mA cm^{-2} for 5-cell stack employing Nafion 117 membrane and E-Tek electrodes with Pt loading of 1.0 mg cm^{-2}

density was investigated. The variation is presented in Table 3. This investigation was carried out consecutively without stopping the VOFC system operation and the indicated times are referenced to the beginning of discharge at 6 mA cm^{-2}. As expected, increasing current density causes a drop in the cell voltages, but a stack voltage of over 4 V is still observed, showing good promise for the VOFC system.

After t = 210 min the stack was allowed to return to a stable OCV of 5.92 V without stopping the electrolyte flow or gas feed. The stack was then continually discharged at a constant current density of 10 mA cm^{-2} until the V(II) electrolyte was completely discharged. The results obtained are presented in Table 4 and plotted in Fig. 6.

One of the cells in the 5-cell VOFC system, Cell 4, occasionally showed a sudden drop in its operating voltage and then suddenly returned to its original voltage. This behaviour was observed through the discharge profile and since knocking the system could sometimes recover the voltage, it was considered to be a contact or gas flow problem. The other 4 cells demonstrated undisturbed operation throughout the discharge verifying that this system can maintain a stable operating characteristic.

The difference between the open circuit voltage and operating voltage at t = 3.7 h was used to estimate the voltage efficiency of the stack and an approximate value of 78.9% was obtained, showing that the stack design and

Table 3 Changes in cell and stack voltages versus discharge current for 5-cell stack employing Nafion 117 membrane and E-Tek electrodes with Pt loading of 1.0 mg cm^{-2}

Time (min)	Current density (mA cm^{-2})	VOFC (V)	Cell 1 (V)	Cell 2 (V)	Cell 3 (V)	Cell 4 (V)	Cell 5 (V)
160	10	4.83	0.986	0.981	0.834	1.045	0.987
174	15	4.35	0.926	0.903	0.734	0.900	0.884

Table 4 Changes in stack voltages versus time at a constant discharge current of 10 mA cm^{-2} for 5-cell stack employing Nafion 117 membrane and E-Tek electrodes with Pt loading of 1.0 mg cm^{-2}

Time (h)	Stack voltage (V)	Cell voltage (V)				
		Cell 1	Cell 2	Cell 3	Cell 4	Cell 5
t = 3.7	OVC = 5.92	1.189	1.177	1.099	1.223	1.235
Discharging at 10 mA cm^{-2}						
3.7	4.67	1.017	0.979	0.857	0.955	0.865
18.6	4.48	0.922	0.829	0.896	1.012	0.822
20.6	4.89	0.967	0.895	0.956	1.167	0.905
22.6	4.76	0.957	0.900	0.968	1.011	0.909
25.6	4.83	0.969	0.897	0.959	1.092	0.908
73.7	4.21	0.874	0.826	0.862	0.943	0.700
92.6	3.52	0.705	0.763	0.759	0.678	0.616
94.3	3.50	0.696	0.752	0.757	0.673	0.617
102.5	3.00	–	–	–	–	–
103.0	2.65	–	–	–	–	–
103.25	1.80	–	–	–	–	–
103.40	2.65	–	–	–	–	–

Times are total time from beginning of original discharge run

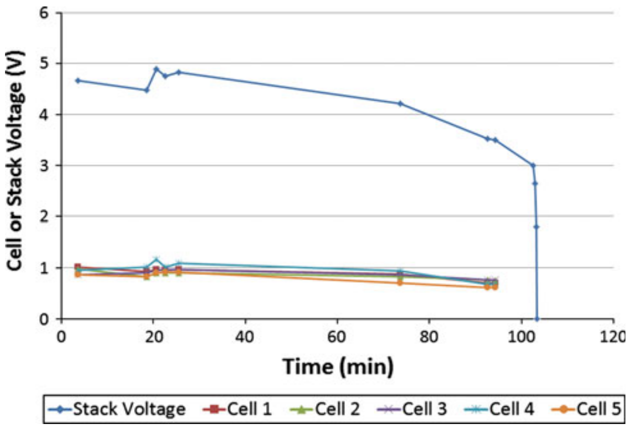


Fig. 6 Stack voltage and cell voltages at a constant discharge current density of 10 mA cm^{-2} for 5-cell stack employing Nafion 117 membrane and E-Tek electrodes with Pt loading of 1.0 mg cm^{-2}

bipolar electrode arrangement used here is very promising in terms of expected overall energy efficiency, although long-term operation may be affected by delamination of the MEA as a result of membrane swelling. A serious technical problem encountered with some of the membrane electrode assemblies tested here was in fact the detachment of the membrane from the electrode assembly due to expansion of the membrane during operation. This is an area that will require further optimization for practical implementation of the redox fuel cell hybrid system.

In addition, the potential for oxygen transfer into the negative half-cell is an inherent property of all membrane fuel cells and is expected to lead to some internal self-discharge during operation, the magnitude of which is a function of the type of membrane used. In the present study, more than 90% active material utilization was observed in some of the cell discharge tests, showing that oxygen diffusion across the membrane should not be a major issue, at least during short-term operation of the cell. A more challenging technical issue is likely to be electrolyte transfer into the gas diffusion electrode during long-term operation and methods to reduce this transfer will need to be investigated further.

5 Conclusions

In this study, a number of cell and membrane electrode assembly designs were developed and tested in a vanadium oxygen fuel cell employing a V(II) negative half-cell solution with an oxygen gas diffusion electrode. A 5-cell VOFC system was operated with Nafion 117 membrane for a total of over 120 h. The cell demonstrated excellent stability without any deterioration in its performance. In some of the earlier designs incorporating the thinner Nafion 112 membrane, vanadium solution penetrated the MEA assembly and permeated out the back of the gas diffusion electrode being detected at the gas outlet.

In the improved design, water build up occurred in the back of the oxygen electrode and naturally drained out of the gas feed port. The thicker Nafion 117 membrane has a lower vanadium ion permeation that reduces the transfer of vanadium ions from the negative half-cell, so even after the 120 h of operation the water that built up behind the gas diffusion electrode was still clear. The higher ohmic resistance of the Nafion 117 membrane was thus offset by the lower vanadium permeation. When fed with pre-saturated oxygen gas pre-heated to 60 °C, however the cell resistance was significantly reduced due to the reduced polarization resistance. Although the cell resistance was still relatively high at 9.8 ohms cm^2, however, when operated at 10 mA cm^{-2}, a voltage efficiency of 78.9% was still obtained with the 5-cell stack.

This latest design was a major step forward in the development of the VOFC system since it demonstrated that a multi cell VOFC stack can be successfully constructed and that a significant weight and volume reduction can be achieved with the total elimination of the positive electrolyte.

As mentioned, the detachment of the membrane from the electrode assembly due to expansion of the membrane during operation, was a significant problem encountered with some of the membrane electrode assemblies tested here. To overcome this problem, the membrane needs to be hydrated and bonded whilst wet to avoid shrinkage on drying followed by expansion on soaking in the electrolyte. This would make the physical bonding of the membrane to the electrode very difficult however. The use of an improved membrane with very low swelling and expansion properties should solve this problem and given the promising results obtained with the VOFC test cells to date, further studies with improved low cost membranes are warranted. Pt catalysts for the oxygen diffusion electrode would also be prohibitively expensive, so non-noble metal catalysts would need to be developed before any commercial application of a hybrid redox fuel cell would be considered for electric vehicles in the future. Since the positive half-cell electrolyte is eliminated in the VOFC system, there are no V(V) thermal precipitation problems as in the conventional VRB, so a much higher operating temperature could be employed to increase the reaction kinetics and the energy efficiency, allowing less expensive catalysts to be potentially developed.

Greater improvements in energy density could also be achieved by replacing the sulphuric acid supporting electrolyte with either HCl or HCl/H_2SO_4 mixtures that have exhibited higher solubilities for the V(III) and V(III) ions [26, 32]. This could potential triple or quadruple the energy density of the hybrid vanadium–oxygen redox fuel cell compared with the original all-vanadium redox flow battery, but further work is needed to optimize this high energy density electrolyte for the VOFC.

In this study, the VOFC was used in fuel-cell mode only and no recharging or regeneration of the negative half-cell electrolyte was considered. In practical systems, recharging could be carried out in a separate electrolytic cell that would reduce the V^{3+} ions in the discharge electrolyte to V^{2+} at the negative electrode, while producing oxygen gas at the positive electrode. This dual battery concept that uses separate cell stacks for the charging and discharging of the electrolytes was proposed by Skyllas-Kazacos et al. in 1988 [33] and has the advantage that the re-charging cell can be optimized for the charging process only, so that dimensionally stable anodes could be used to provide long life during continuous operation. Given the increasing interest in electric vehicles, the possibility of using a power source that can be re-fuelled by simply filling the tank with recharged solution and then using off-peak electricity to regenerate the spent solutions is a very attractive concept that warrants further development.

Acknowledgments This work was originally funded by the New South Wales Department of Minerals and Energy through the State Energy Research and Development Fund.

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