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State of charge monitoring methods for vanadium redox flow battery control

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ABSTRACT

During operation of redox flow batteries, differential transfer of ions and electrolyte across the membrane and gassing side reactions during charging, can lead to an imbalance between the two half-cells that results in loss of capacity. This capacity loss can be corrected by either simple remixing of the two solutions, or by chemical or electrochemical rebalancing. In order to develop automated electrolyte management systems therefore, the state-of-charge of each half-cell electrolyte needs to be known. In this study, two state-of-charge monitoring methods are investigated for use in the vanadium redox flow battery. The first method utilizes conductivity measurements to independently measure the state-of-charge of each half-cell electrolyte. The second method is based on spectrophotometric principles and uses the different colours of the charged and discharged anolyte and catholyte to monitor system balance and state-of charge of each half-cell of the VRB during operation.

1. Introduction

Redox flow batteries have many technical benefits over other energy storage systems as well as an excellent combination of energy efficiency, capital cost and life cycle costs compared with other technologies [1]. While the redox flow cell concept has been around for close to 40 years with several systems evaluated by various groups around the world, only the Vanadium Redox Flow Battery (VRB) [2–16] has to date, reached commercial fruition. The VRB was pioneered at the University of New South Wales in Australia where it was taken from the initial concept stage in 1984 through the development and demonstration of several 1–4 kW prototypes in stationary and electric vehicle applications during the late 1980s and 1990s [13,14] followed by several demonstrations and field trial by Mitsubishi Chemical Corporation and Sumitomo Electric Industries in the late 1990s to early 2000s [15,16].

The VRB has unique and highly competitive features compared to alternative battery solutions, including:

- Employs the same electrolyte solution in both half-cells, thereby eliminating cross-contamination and electrolyte maintenance problems faced by all other redox flow batteries
- Ability to scale-up the battery storage capacity at low capital cost, by simply increasing the electrolyte volume and tank size
- Indefinite life of the vanadium electrolytes reduces replacement costs and minimizes waste
- High energy efficiencies possible (up to 80%)
- Simple control and monitoring systems
- Long cycle life
- Minimal safety issues
- Can be fully discharged without harming the battery

As with all electrochemical systems however, a number of side reactions can occur during operation that can cause loss of capacity over extended charge–discharge cycling. These include:

1. Air oxidation of the V(II) ions in the negative half-cell causing an imbalance between the positive and negative electroactive species and a subsequent loss of capacity.
2. Gassing side reactions during charging – in particular hydrogen evolution at the negative electrode, leading to an imbalance between the positive and negative electroactive species and a subsequent loss of capacity.
3. Differential transfer of vanadium ions from one half-cell to the other causing a build up in one half-cell and a corresponding dilution in the other.
4. Volumetric transfer of electrolyte from one half-cell to the other due to differential pressure drop across the membrane.

While any capacity loss caused by Processes (3) and (4) can be readily corrected by simple periodic electrolyte remixing that rebalances the electrolyte compositions and liquid levels in each reservoir, capacity losses by Processes (1) and (2) can only be corrected by chemical or electrochemical rebalancing of the oxidation states of the two half-cell electrolytes. Suitable state-of-charge monitoring methods are therefore needed to detect any imbalances

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in the individual electrolyte oxidation states so that appropriate correction procedures can be applied to restore any loss of capacity.

Traditionally, open circuit cells are used to monitor the state-of-charge of a cell by using the Nernst Equation to relate the reversible (or open-circuit potential) to the logarithm of the redox reaction ion ratio (corresponding to state-of-charge):

Although the open-circuit cell voltage (OCV) can be used as an indication of the overall cell state of charge (SOC) through the application of the Nernst equation, this will only be accurate if the system is balanced. If the electrolytes become unbalanced, however, it is not be possible to determine the electrolyte imbalance from the open-circuit voltage, nor will the cell SOC be accurately indicated by the OCV. Ideally, therefore, each of the half-cell electrolyte potentials should be monitored so that the SOC of each half-cell electrolyte can be independently monitored.

Theoretically an inert indicator electrode could be utilized in each half-cell electrolyte reservoir, however, in a large scale redox flow cell system the use of such an electrode would be impractical since solution potential measurement also requires a stable reference electrode potentia1. Reference electrodes are however inherently unreliable due to a large number of interferences that can lead to drifts in the measured potential. Furthermore, the solution potential changes only slightly over a wide range of states-of-charge so that sensitivity is poor.

Two alternative forms of SOC monitoring have thus been investigated, one which utilizes conductivity measurements and the other, absorption measurements based on spectrophotometric principles, using the different colours of the charged and discharged anolyte and catholyte to allow monitoring of system balance and state-of charge of each half-cell of the VRB during operation. In the negative half-cell of the VRB, the following colour transitions occur during charge–discharge cycling:

$$\underset{\text{violet}}{V(II)} \Leftrightarrow \underset{\text{green}}{V(III)} + e$$

while in the positive half-cell:

$$\underset{\text{yellow}}{V(V)} + e \Leftrightarrow \underset{\text{blue}}{V(IV)}$$

Electrolyte conductivity can also be used to continuously monitor state of charge and regulate charging and discharging between desired limits. Since electrolyte composition varies during charge–discharge cycling, it should be possible to monitor individual half-cell solution conductivities and correlate these to the SOC or oxidation state of each half-cell.

2. Experimental

In this study, vanadium solutions of compositions corresponding to different negative and positive half-cell electrolyte states-of-charge, were prepared by the electrolysis of 2 M vanadyl sulfate solutions in different concentrations of H_2SO_4 supporting electrolyte. The vanadyl sulfate stock solution was placed into both halves of an electrolysis cell (with twice the volume used on the positive side) and electrolysed at a current density of 20 mA cm^{-2} to produce 2 M V(V) in the positive half-cell and 2 M V(II) in the negative.

During electrolysis, the following reactions take place:

In the positive half-cell:

$$VO^{2+} + H_2O \rightarrow VO_2^{+} + 2H^{+} + e \quad (1)$$

In the negative half-cell:

$$VO^{2+} + 2H^{+} + e \rightarrow V^{3+} + H_2O \quad (2)$$

followed by:

$$V^{3+} + e \rightarrow V^{2+} \quad (3)$$

The end-point in the electrolysis was taken as the time when the positive and negative electrolytes turned yellow and violet respectively, verifying that the solutions were close to 100% V(V) and V(II).

A portion of each of the 2 solutions was removed from the cell and the remaining volumes were then pumped through the cell to allow the discharge reactions to occur to produce a green V(III) solution in the negative half-cell and a blue V(IV) solution in the positive.

The resultant solutions were mixed in different V(II):V(III) and V(V):V(IV) ratios to simulate a range of electrolyte states of charge. Solutions of different vanadium and total sulfate concentrations were prepared with this method and used for the conductivity and UV–vis spectroscopic measurements.

The UV–vis spectra of the vanadium solutions were measured using a Varian Superscan 3 double beam spectrophotometer with a scan rate of 200 nm min^{-1}.

Conductivities were measured with a Type CDM2e Radiometer conductivity meter with a Type CD104 Radiometer conductivity probe. The apparatus was calibrated using a 0.05% NaCl solution and the probe was allowed to equilibrate for 5 min or until steady state was reached.

3. Results and discussion

3.1. Electrolyte conductivity as a function of state-of-charge

The conductivities of V(V), V(IV), V(III) and V(II) solutions were measured for different vanadium and total sulfate concentrations using a Radiometer CDM2e conductivity meter and the results are presented in Table 1 for a temperature of 22 ± 1 °C.

From the results summarized in Table 1, it can be seen that of all the vanadium ions, V(V) has the highest conductivity in H_2SO_4 solutions. This is mainly due to the higher proton concentration in the V(V) solution compared with the corresponding V(IV), V(III) and

Table 1
Effect of composition on conductivity. Temperature = 22° ± 1° C.

Vanadium ion	Vanadium ion concentration (M) ±0.1 M	Total sulfate concentration (M) ±0.1 M	Conductivity (mS cm^{-1}) ±5%
V(V)	2.0	5.0	365
	2.0	4.5	350
	2.0	4.0	335
	1.5	4.0	385
	1.0	4.0	420
	0.5	4.0	440
V(IV)	2.0	5.0	200
	2.0	4.5	200
	2.0	4.0	175
	1.5	4.0	229
	1.0	4.0	285
	0.5	4.0	340
V(III)	2.0	5.0	220
	2.0	4.5	190
	2.0	4.0	160
	1.5	4.0	210
	1.0	4.0	270
	0.5	4.0	339
V(II)	2.0	5.0	240
	2.0	4.5	230
	2.0	4.0	210
	1.5	4.0	260
	1.0	4.0	320
	0.5	4.0	370