

Effects of battery design, environmental temperature and electrolyte flowrate on thermal behaviour of a vanadium redox flow battery in different applications



Yitao Yan, Maria Skyllas-Kazacos*, Jie Bao

School of Chemical Engineering, UNSW Australia, Sydney, NSW 2052, Australia

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ABSTRACT

This paper examines the effect of flowrate, cell number, tank dimension and environment temperature on the thermal behaviour of the vanadium redox flow battery. Simulations are carried out under a power arbitrage scenario for two different types of membranes. It was found that at high flowrates the thermal behaviour of the stack is similar to that of the storage tanks. Increasing the number of cells in the stack does not change the shape of the general thermal gradient across the cells, but changing the tank dimensions can affect the system temperature significantly. The environment temperature has a significant impact on the system thermal behaviour as does the types of membrane used. This study shows that by altering the parameters, the thermal behaviour of the system can be regulated and even, in some cases, controlled within desirable ranges to prevent vanadium salt precipitation at temperature extremes.

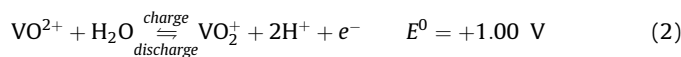
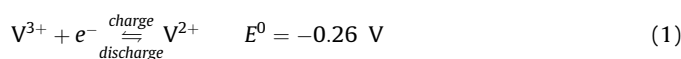
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1. Introduction

Large-scale cost effective energy storage has become one of the most pressing issues in the world today due to the rapid development of renewable, yet unstable, forms of energy. Of the currently available energy storage technologies, the vanadium redox flow battery (VRFB) developed by Skyllas-Kazacos and co-workers [1] is regarded as the technology with the greatest potential to facilitate the more widespread implementation of renewable energies such as wind and solar. The energy efficiency of the first 1 kW VRFB prototype fabricated by the UNSW group in the early 1990s was measured as 90% [2] and numerous groups have since continued researching and further developing the system both in the laboratory and in the large-scale field trials. Several companies are now manufacturing commercial VRFB systems in Japan, Germany, USA and China, and many large-scale commercial VRFB systems have been successfully implemented in a wide range of stationary energy storage applications around the world.

Using V^{2+}/V^{3+} as anolyte [3], and VO^{2+}/VO_2^+ redox couple as catholyte [4], the VRFB overcomes the problem of cross-

contamination, which is an inherent, unavoidable problem in all other redox flow battery (RFB) systems with ions of different elements in the anolyte and catholyte. The general chemical reaction in the cells can be described by the following primary electrode reactions:



where reaction (1) is the reaction in the negative half-cell and reaction (2) takes place in the positive half-cell with an overall standard cell potential of 1.26 V. Under actual cell conditions however, the cell potential at 50% state-of-charge (SoC) has been measured as 1.35–1.40 V for vanadium concentrations of 1.6–2.0 M [5].

Despite its superiority over other types of RFBs, however, during the operation of the VRFB system, several issues can arise that require consideration for optimal performance and cycle life. Although the use of the same ions in both half-cells overcomes problems of cross-contamination, self-discharge resulting from diffusion of the vanadium ions across the membrane can still lead to heat generation and thermal issues that need to be managed. If

* Corresponding author.

E-mail address: m.kazacos@unsw.edu.au (M. Skyllas-Kazacos).

| | |
|---------------|--------------------------------------|
| ΔH | heat of reactions |
| A | amplitude of oscillation |
| c | concentration |
| C_p | specific heat capacity |
| D | prefactor |
| d | diffusivity coefficient |
| E_a | activation energy |
| F | Faraday's constant |
| h | convective heat transfer coefficient |
| i | current |
| k | thermal conductivity |
| l | tank height |
| N | cell number |
| <i>outlet</i> | outlet flow |
| Q | flowrate |
| Q_f | flow factor |
| R | gas constant |
| r | tank radius |
| S | area |
| T | temperature |
| t | time |
| U | overall heat transfer coefficient |
| V | volume |

Greek letter

| | |
|----------|---------------------|
| ω | cell resistance |
| ρ | electrolyte density |
| θ | thickness |

Superscript

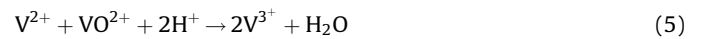
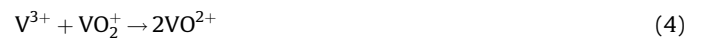
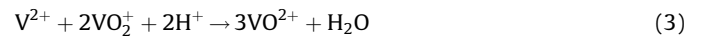
| | |
|-----|----------------------------------|
| + | positive half-cell |
| – | negative half-cell |
| m | oxidation number of vanadium ion |
| s | stack |
| t | storage tank |

Subscript

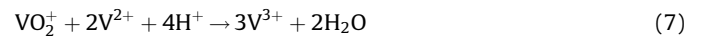
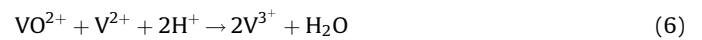
| | |
|----------------------|-----------------------------------|
| 0 | initial |
| 1 | first cell |
| 2 | V^{2+} |
| 3 | V^{3+} |
| 4 | VO^{2+} |
| 5 | VO_2^+ |
| 10 | 10th cell |
| $II \rightarrow III$ | reaction (5) |
| $III \rightarrow IV$ | reaction (4) |
| $IV \rightarrow III$ | reaction (6) |
| $V \rightarrow III$ | reaction (7) |
| <i>air</i> | environment |
| <i>base</i> | base of the storage tank |
| c | centre |
| <i>cell</i> | cell |
| <i>in</i> | inner surface of the storage tank |
| <i>inlet</i> | inlet flow |
| <i>mem</i> | membrane |
| n | n th cell |
| <i>out</i> | outer surface of the storage tank |
| s | stack |

| | |
|-------------|--------------------------|
| <i>side</i> | side of the storage tank |
| t | storage tank |
| V | vanadium |
| x | x direction |
| y | y direction |
| z | z direction |

the rate of diffusion of the different vanadium ions varies considerably, there could also be a gradual build-up of vanadium ions in one half-cell and dilution in the other, leading to capacity loss. Although this type of capacity loss can be readily restored by periodic remixing of the two half-cell electrolytes, it is important to be able to predict these changes for good electrolyte management. In VRFB, the main self-discharge reactions in the positive half-cell are caused by the diffusion of V^{2+} and V^{3+} ions across the membrane from the negative half-cell:



In the negative half-cell, diffusion of VO^{2+} and VO_2^+ ions from the positive side gives rise to the following self-discharge reactions:



The self-discharge process can be separated into 3 stages [6], namely

- i. Normal self-discharge when all four vanadium ions are present and can diffuse across the membrane.
- ii. Further reactions when V^{2+} or VO_2^+ is fully depleted in its respective half-cell electrolyte.
- iii. Ion diffusion of V^{3+} and VO^{2+} until both half-cell electrolytes reach an equilibrium 50:50 mixture of the two ions (often referred to as $V^{3.5+}$).

It should be noted that in stage iii, there is no reaction occurring that releases heat, so ignoring any heat of mixing, no further temperature change would take place during stage iii.

The problem with self-discharge is not only the loss of coulombic efficiency and energy storage capacity, but also heat generation by these reactions that can lead to increases in stack and electrolyte temperatures that can in turn cause potential membrane damage of membrane and possible VO_2^+ thermal precipitation according to the endothermic reaction shown in Eq. (9).



Other factors that lead to capacity loss include air oxidation of V^{2+} to V^{3+} in the negative half-cell [5,7], and hydrogen and oxygen evolution during charging [5,8–11]. This type of capacity loss cannot be restored by simple electrolyte remixing, and requires either chemical or electrochemical rebalancing [5]. Although there are many ways to minimise or overcome these potential problems

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