

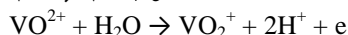
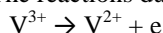
Kinetics of the Redox Reactions in the Vanadium Redox Flow Battery

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Vanadium redox flow batteries (VRFBs) are a promising technology to meet energy storage requirements for large scale and remote area applications¹. Flow batteries offer a long cycle life² and the energy capacity can be scaled separately from the power capacity. This design flexibility makes them suitable for a wide range of applications. VRFBs have the additional advantage of having the same element on both sides of the membrane which eliminates cross-contamination issues that arise in mixed-element flow batteries. As a result electrolyte maintenance issues are reduced; in theory, the electrolyte is indefinitely reusable.

In a VRFB the electroactive species are dissolved in the electrolyte. The redox couples are V(II)/V(III) in the negative half-cell and V(IV)/V(V) in the positive half cell. The reactions during charging may be written as:



The negative half-cell reaction appears to be a simple one-electron transfer reaction while the positive half-cell reaction appears to involve bond breaking. Thus the kinetics would be expected to be faster at the negative electrode than at the positive. However, in actual flow cells, the overpotential is much larger at the negative electrode than at the positive³.

Several authors have performed cyclic voltammetry experiments on glassy carbon electrodes and concluded that the electrode kinetics for V(IV)/V(V) are faster than for V(II)/V(III)⁴⁻⁶. However other authors have reported on the basis of steady state polarization experiments at rotating disk⁷ and fixed carbon/plastic composite electrodes⁸ that the electrode kinetics for V(II)/V(III) are faster than for V(IV)/V(V). Using cyclic voltammetry Yamamura et al.⁹ concluded that the electrode kinetics for V(IV)/V(V) are faster than for V(II)/V(III) at plastic formed carbon electrodes but slower at pyrolytic graphite electrodes. Similarly, Wu et al.¹⁰ reported that the relative rates of the V(IV)/V(V) and V(II)/V(III) electrode kinetics depend on the nature of the carbon electrode. Thus, the overpotentials observed at the electrodes of actual flow cells have not been adequately explained in terms of the V(II)/V(III) and V(IV)/V(V) electrode kinetics.

We have conducted charge-discharge, cyclic voltammetry and steady state polarization experiments in order to better understand the electrode reactions and to explain the observed overpotentials during charge and discharge.

Charge-discharge experiments were conducted using a 'sandwich' type flow cell. Electrodes consisted of carbon felt (10 mm in thickness) separated by 180 μm Nafion® 117 membrane supplied by Dupont. The electrodes were 80 mm x 20 mm and were contacted by carbon-filled

polymer backplates supplied by Bac2 Ltd. Both anolyte and catholyte were circulated at a flow rate of 0.45 $\text{cm}^3 \text{s}^{-1}$ by a dual-head peristaltic pump from glass reservoirs thermostatted at 25°C and purged with nitrogen. Potentials were measured relative to saturated Hg/Hg₂SO₄ reference electrodes. The flow cell was used to evaluate the charge-discharge characteristics of each half cell at a range of electrolyte concentrations. It was also used to prepare electrolyte solutions at different states of charge, i.e. different V(II):V(III) and V(IV):V(V) ratios.

Cyclic voltammetry and steady state polarization curves were carried out at stationary carbon electrodes in a three-electrode cell with a carbon or platinum counter electrode and a saturated Hg/Hg₂SO₄ reference electrode. Various carbon materials were investigated (carbon felt, glassy carbon and graphite) in different concentrations of electrolyte and at various states of charge. Results obtained at stationary electrodes under the various conditions investigated will be discussed and compared with those obtained under corresponding conditions in the flow cell.

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