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The electrolyte monitoring of a vanadium redox flow battery

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Redox flow batteries (RFBs) have received increasing attention over the last few years as a viable energy storage technology. The different chemistries and features of the various RFBs currently under development have been reviewed [1]. The all-vanadium redox flow battery (VRFB) containing V(II)/V(III) and V(IV)/V(V) redox couples in the negative and positive half-cell electrolytes, respectively [2, 3], is the most widely studied RFB [4, 5]. A series of carbon felts was examined by cyclic voltammetry to investigate their suitability as an electrode material for the all-vanadium redox flow battery. A commercially supplied vanadium electrolyte of unknown concentration was analyzed by UV-visible spectroscopy and was shown to contain VO^{2+} and V^{3+} ions in a ratio of 4.8:1 with a total vanadium concentration of 1.5 mol dm^{-3} in 4 mol dm^{-3} H_2SO_4 (Figure 1). A unit laboratory redox flow battery (100 cm^2 membrane area) was assembled using carbon felts and planar carbon feeders as the positive and negative electrodes with a Nafion® 115 proton exchange membrane. Charge-discharge experiments using both 1.5 mol dm^{-3} and 1.1 mol dm^{-3} vanadium electrolytes at volumetric flow rates in the range of 0.5 to 3 cm^3 min^{-1} showed that extremely high charge efficiencies are possible, indicating that the rates of gas evolution reaction are slow under the practical conditions considered (Figure 2). At a vanadium concentration of 1.1 mol dm^{-3}, the best flow rate was found to be in the range 1.5–2 cm^3 min^{-1}, while at 1.5 mol dm^{-3}, the best performance (highest overall efficiency) was found to be at 1.5 cm^3 min^{-1}. Higher flow rates had a detrimental effect of the efficiencies, particularly the charge efficiency. In fact, the differences in the efficiency values between 0.5 and 1.5 m cm^{3}min^{-1} were small (Table 1), implying that operating the system at 0.5 cm^3 min^{-1} would be cost effective when the total power consumption, including for the auxiliary components, is taken into account. The 1.1 mol dm^{-3} solution also exhibited significantly higher concentration polarization up to a reasonably high flow rate. Operating with this concentration therefore requires more power to achieve good performance and avoid component degradation as a result of high local potentials. At a constant current density charge and discharge of 100 mA cm^{-2} for 45 minute half-cycles (and <30 cycles), the typical voltage efficiencies were 65 %.

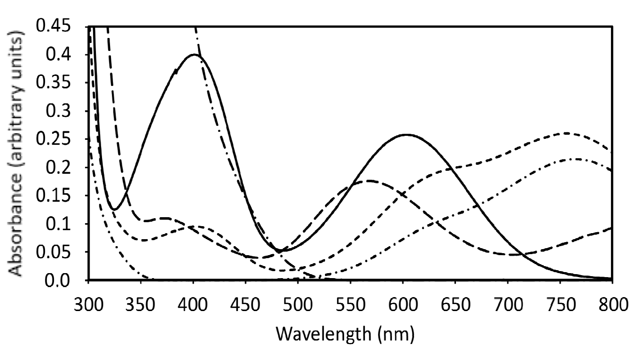

Figure 1: UV-visible spectra for the vanadium solutions obtained during the electrochemical reduction of dissolved V_2O_5 (long dashed dotted line = VO_2^+, short dashed dotted line = VO^{2+}, solid line = V^{3+}, long dashed line = V^{2+} and short dashed line = commercially supplied vanadium solution).

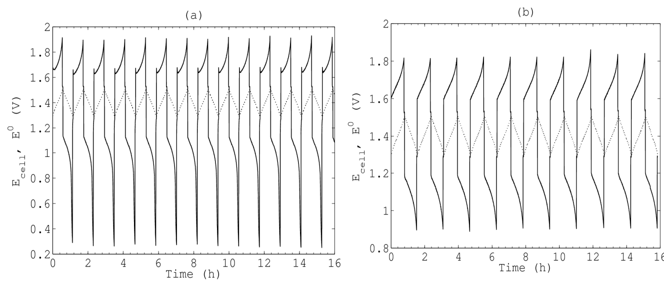

Figure 2: Charge-discharge curves (cycles 1 - 12) using an electrolyte with (a) 1.1 mol dm^{-3} and (b) 1.5 mol dm^{-3} vanadium ions in 4 mol dm^{-3} H_2SO_4. The current density was maintained at 100 mA cm^{-2} during charge and discharge and the flow rate was 1 cm^3 min^{-1}. Cut-off values for the open-circuit cell voltage of 1.5 V during charge and 1.3 V during discharge were used to define the charge and discharge times, respectively. Solid line: cell voltage; dashed line: electrolyte monitoring open-cell voltage; dotted line: current density. The cell contained 100 x 100 x 4 mm 'GFA' felt electrodes in each half-cell compartment.

Table 1: Summary of results obtained from charge/discharge experiments on the VRFB at 1.1 mol dm^{-3} and 1.5 mol dm^{-3} vanadium ion concentrations in 4 mol dm^{-3} H_2SO_4 at 23 °C and at controlled flow rates (0.5, 1, 1.5, 2.0 and 3.0 cm^3 min^{-1}). All results were obtained at a constant current density of 100 mA cm^{-2} such that the charge efficiency is nearly 100 %.

Vanadium concentration (mol dm^{-3})	**Volumetric flow rate (cm^3 min^{-1})**	**% Voltage efficiency**	**% Energy efficiency**
1.1	0.5	44	43
	1.0	55	55
	1.5	59	59
	2.0	61	61
	3.0	61	61
1.5	0.5	65	64
	1.0	65	65
	1.5	66	67
	2.0	65	66
	3.0	63	63

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