

Short communication

Novel vanadium chloride/polyhalide redox flow battery

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Abstract

This paper describes a novel redox flow cell which employs a polyhalide solution in the positive half-cell electrolyte and a vanadium(II)/vanadium(III) chloride redox couple as the negative half-cell electrolyte. During charging, the bromide ions in the positive half-cell are considered to undergo oxidation to the polyhalide ion Br_2Cl^- ; the formal potential of this couple is about 0.8 V versus the saturated calomel electrode (SCE). When combined with a formal potential of around -0.5 V versus SCE for the V(II)/V(III) coupled in the chloride supporting electrolyte, an overall cell potential of approximately 1.3 V would be expected for the vanadium chloride/polyhalide redox flow cell.

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1. Introduction

A redox flow cell is an electrochemical system which allows energy to be stored in two solutions that contain different redox couples. These couples have electrochemical potentials which are sufficiently separated from each other to provide an electromotive force to drive the oxidation–reduction reactions required to charge and discharge the cell. Among the redox flow cells developed to date, the all-vanadium redox flow cell has shown long cycle-life and high energy efficiencies of over 80% in large installations of up to 500 kW [1–6]. Most of the advantages of the vanadium redox flow battery are due to the use of the same element in both the half-cells, which avoids problems of cross-contamination of the two half-cell electrolytes during long-term use.

Given its performance characteristics the all-vanadium redox flow battery is well suited to stationary applications but, to date, the relatively low specific energy of $25\text{--}35$ Wh kg^{-1} has limited its use in electric vehicle or other mobile applications. The specific energy of a redox flow battery is related to the concentration of the redox ions in solution, to the cell potential and to the number of electrons transferred during discharge per mole of active redox ions. In the case of the all-vanadium redox flow cell, the maximum vanadium ion concentration that can be employed for operation over a wide temperature range is typically 2 M or less. This concentration represents the solubility limit of the

V(II) and/or V(III) ions in the sulfuric acid supporting electrolyte at temperatures below 5°C and the stability of the V(V) ions at temperatures above 40°C [7,8]. Although 3 M vanadium solutions could be employed over a narrower temperature range of $15\text{--}40^\circ\text{C}$, this still represents a specific energy of 35 Wh kg^{-1} that is considered too low for most electric-vehicle applications.

Laboratory studies with hydrochloric acid supporting electrolyte have shown that V(II) and/or V(III) ion concentrations as high as 4 M can be achieved in a chloride system [9]. The acid is, however, unsuitable as a supporting electrolyte for the positive half-cell of the all-vanadium redox battery. This is due to the fact that V(V) ions are reduced by the chloride ion and give rise to the evolution of chlorine gas and the formation of V(IV) [2]. If an alternative redox couple could be employed in the positive half-cell electrolyte, the use of the higher specific energy $\text{VCl}_2/\text{VCl}_3$ couple would be feasible for the negative half-cell solution. To minimize cross-contamination problems, a chloride-based positive half-cell electrolyte would be preferred.

Various types of polyhalide ions are known to exist and are formed by the interaction between a halogen molecule and a halide ion. For example, the reaction between Br_2 and Cl^- produces the Br_2Cl^- ion, while Cl_2 dissolved in a Br^- solution produces the Cl_2Br^- ion [10]. These species are the polyhalide ion equivalents of the Br_3^- or I_3^- species and are characterized by high oxidation potentials. In fact, the $\text{Br}^-/\text{Br}_3^-$ redox couple is employed in the positive half-cell of the sulfur–bromine redox flow cell developed by Innogy Plc in the UK [11]. While the $\text{Br}^-/\text{Br}_3^-$ redox couple could

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be used in conjunction with the $\text{VCl}_2/\text{VCl}_3$ couple for a new redox flow cell combination, it is preferable to employ a chloride-based couple to minimize cross-contamination problems during operation of the cell.

A new V/polyhalide redox flow cell is thus proposed and employs $\text{VCl}_2/\text{VCl}_3$ in the negative half-cell electrolyte and the $\text{Br}^-/\text{ClBr}_2^-$ couple in the positive half-cell [10]. Cyclic voltammetry is used to study the electrochemical reversibility of the $\text{Br}^-/\text{ClBr}_2^-$ couple, and the charge–discharge performance of a small V/polyhalide test cell is reported.

2. Experimental

Cyclic voltammetry was conducted using a three-electrode cell which comprised a graphite rod embedded in epoxy resin as working electrode (6 mm diameter), with a graphite rod and saturated calomel electrode (SCE) as counter and reference electrodes, respectively. The voltammograms were obtained with the aid of a Model 273 EG&G PAR potentiostat. Cell cycling tests were performed on small test cells which employed graphite felt electrodes contacted against two glassy carbon sheets that acted as current-collectors. Electrical contact was made via two copper plates that were compressed against the glassy carbon plates at each end of the cell.

The two half-cell electrolytes were separated by a sheet of Nafion 112 cation-exchange membrane to prevent the bulk mixing of the two solutions as they were pumped through the cell.

Two Iwaki pumps (Japan) were used to pump each half-cell electrolyte through the corresponding half-cell cavity where the charge–discharge reactions occurred. A Model GPR-1810H GW constant-current power supply connected

to a purpose-built battery controller was employed for the charge–discharge cycling experiments.

3. Results and discussion

A series of cyclic voltammograms obtained at a scan rate of 0.02 V s^{-1} on a graphite electrode in solutions containing 2 M VCl_2 with various concentrations of total Cl^- is shown in Fig. 1. Increasing the chloride ion concentration appears to shift the peak potentials, but an anodic peak is observed at a potential of around -0.52 V in the 8.48 M Cl^- supporting electrolyte, while the corresponding cathodic peak appears at approximately -0.58 V . The formal potential of the V(II)/V(III) couple is thus seen to be at around -0.58 V versus SCE, which would make this couple suitable for use in the negative half-cell of a redox flow battery. Another favorable feature is the absence of any significant hydrogen evolution current at potentials below the V(III) reduction peak. This is also suitable for redox flow cell applications since it indicates that there will not be serious gassing problems at the negative electrode during charging when employing the $\text{VCl}_2/\text{VCl}_3$ couple. Thus, it is evident that the $\text{VCl}_3/\text{VCl}_2$ has adequate reversibility for use in the negative half-cell electrolyte for the proposed redox flow cell.

A series of cyclic voltammograms obtained in solutions of 1.0 M HCl (lower curve), $1.0 \text{ M HCl} + 0.27 \text{ M NaBr}$ (middle curve) and $1.0 \text{ M HCl} + 2.5 \text{ M NaBr}$ (upper curve) is presented in Fig. 2. Scanning the electrode in the positive direction in HCl is seen to give rise to an anodic current associated with Cl_2 and/or O_2 evolution. No cathodic peak is observed on the reverse scan. This shows that no electrochemically reversible products are produced at the electrode surface during the positive scan. On the other hand,

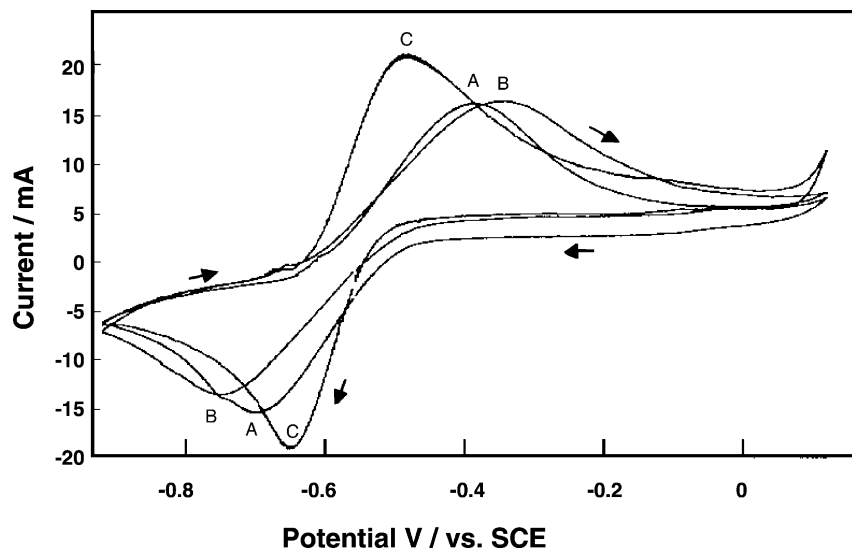


Fig. 1. Cyclic voltammograms at glassy carbon electrode in 2 M V(II) solutions containing various chloride ion concentrations, $[\text{Cl}^-]$: (A) 5 M ; (B) 6.7 M ; (C) 8.5 M .

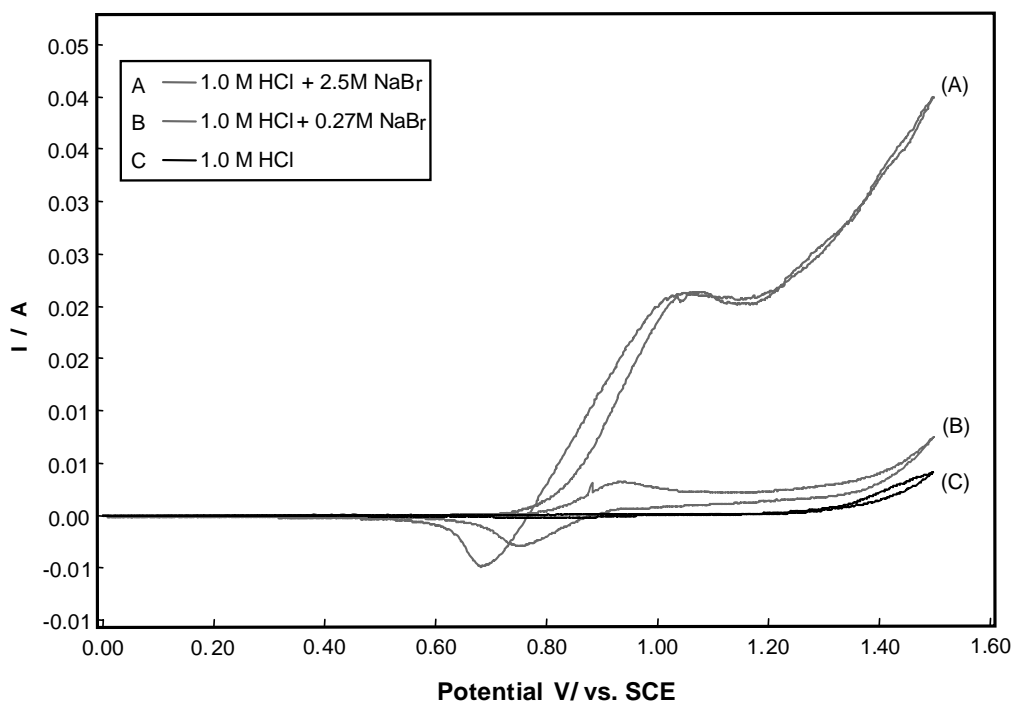
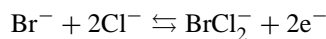
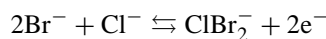


Fig. 2. Cyclic voltammograms in 1.0 M HCl (lower curve), 1.0 M HCl + 0.27 M NaBr (middle curve) and 1.0 M HCl + 2.5 M NaBr (top curve).

when NaBr is present in the electrolyte, anodic and cathodic peaks appear in the forward and reverse scans, respectively. This indicates that a reversible redox couple reaction with a formal potential of approximately 0.85 V is occurring at the electrodes in the HCl–HBr mixture. When the concentration of the NaBr is increased to 2.5 M, the height of the anodic peak is seen to increase significantly. Under these conditions, the Br^- ions are oxidized at the electrode surface to produce an electrochemically active product which can be reduced back to Br^- ions on the reverse scan. It can, therefore, be assumed that the reactions can be represented by:



or



The relatively reversible nature of these reactions suggests that the $\text{Br}^-/\text{ClBr}_2^-$ and/or $\text{Cl}^-/\text{BrCl}_2^-$ couples could be suitable candidates for use in the positive half-cell electrolyte of the proposed redox flow cell.

A vanadium/polyhalide cell was thus set-up with glassy carbon sheets as the current-collectors and graphite felt as the electrode material in both the half-cells. A piece of Nafion 112 membrane was used as separator between the two half-cells and 50 ml of each of the two half-cell electrolytes was placed in the two electrolyte containers. The composition of the negative half-cell electrolyte was 1 M VCl_3 in 1.5 M HCl, while that of the positive half-cell electrolyte was 1 M NaBr in 1.5 M HCl. The solution were pumped through

the cell and a charging current of 20 mA cm^{-2} was applied. When the cell voltage began to increase rapidly, the charging current was switched off and the cell allowed to discharge at a current density of 20 mA cm^{-2} . A typical plot of cell voltage versus time obtained for a full charge–discharge cycle is given in Fig. 3. From this plot, the Coulombic and voltage efficiency values were calculated as 83 and 80%, respectively.

The proposed charge–discharge reactions of the V/polyhalide redox cell can be described as follows:

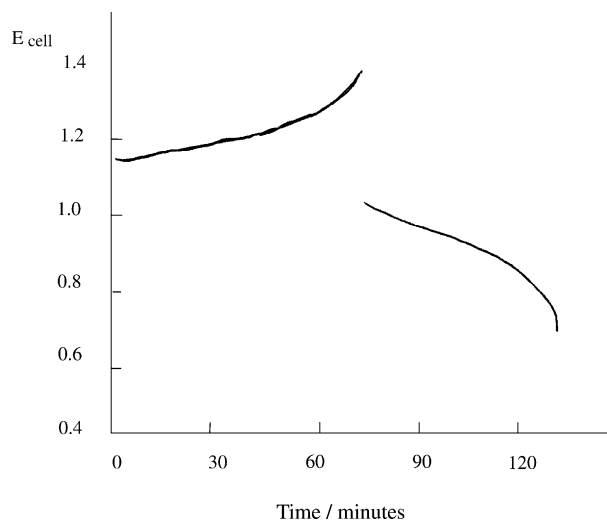
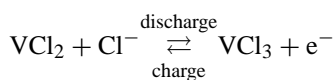
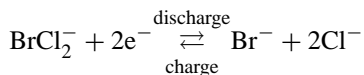


Fig. 3. Charge–discharge curve for V/polyhalide redox cell employing 1 M VCl_3 in 1.5 M HCl in negative half-cell and 1 M NaBr in 1.5 M HCl in positive half-cell.

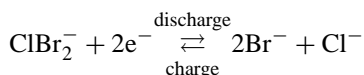
Negative:



Positive:



or



While the cell component materials, electrolyte composition and cell design have yet to be optimized, the above results demonstrate that a novel V/polyhalide redox flow cell is technically feasible and warrants further investigation.

4. Conclusions

A novel V/polyhalide redox flow cell which employs the $\text{VCl}_3/\text{VCl}_2$ couple in the negative half-cell electrolyte and the $\text{Br}^-/\text{ClBr}_2^-$ couple in the positive half-cell is reported. Coulombic and voltage efficiencies of 83 and 80%, respectively, are obtained in a small laboratory cell that has a Nafion 112 membrane and graphite felt electrodes compressed against glassy carbon current-collectors. Further work is currently underway to test the cell with higher vanadium ion concentrations in solutions of various bromide to chloride ratios so that higher specific energies can be achieved. To date, only short-term cycling has been conducted, so it is not possible to predict the cycle-life of this cell. The long-term effect of electrolyte cross-contamination by ion transfer across the membrane has to be established, as well as the chemical stability of the membrane in the bromine–polyhalide mixture. A range of graphite felt and

membrane materials are presently being evaluated over extended cycling periods to determine the long-term performance of the cell and to optimize the Coulombic, voltage and energy efficiencies.

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