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Towards an all-vanadium redox flow battery with higher theoretical volumetric capacities by utilizing the VO^{2+}/V^{3+} couple

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ABSTRACT

An all-vanadium redox flow battery with V(IV) as the sole parent active species is developed by accessing the VO^{2+}/V^{3+} redox couple. These batteries, referred to as V4RBs, possess a higher theoretical volumetric capacity than traditional VRBs. Copper ions were identified as an effective additive to boost the battery performance.

1. Introduction

Q2 With increasing demands on renewable energy deployments and electric grid modernizations, redox flow batteries (RFBs) have recently attracted a great wealth of research interests [1–3]. All-vanadium redox flow batteries (VRBs), first invented by the Skyllas-Kazacos group [4], are perhaps the most well-developed and promising RFB system, and have already been deployed at large scale [5,6]. Tremendous research efforts have been invested towards further developments of the system. For example, by optimizing the electrolyte solution chemistry, the energy density in VRBs can be improved by a 70% margin, together with a 80% increase in temperature range of stable operation [7].

In VRBs, four different oxidation states of the same element are employed: V (V, IV, III, and II). As shown in Fig. 1, in strong acids, the corresponding species of these oxidation states constitute three redox couples with a single electron transfer: VO_2^+/VO^{2+}, $VO^{2+}/V^{3+}$and V^{3+}/V^{2+}. Conventional VRBs utilize the VO_2^+/VO^{2+} and V^{3+}/V^{2+} couples to undergo the following electrochemical reactions, and have a theoretical cell voltage of 1.25 V:

$$\text{Cathode half} - \text{cell}: VO_2^+ + 2H^+ + e^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\longleftrightarrow}} H_2O + VO^{2+}$$

$$\text{Anode half} - \text{cell}: V^{2+} \underset{\text{Charge}}{\overset{\text{Discharge}}{\longleftrightarrow}} V^{3+} + e^-$$

$$\text{Overall}: VO_2^+ + V^{2+} + 2H^+ \underset{\text{Charge}}{\overset{\text{Discharge}}{\longleftrightarrow}} V^{3+} + VO^{2+} + H_2O$$

In traditional VRB systems, the VO^{2+}/V^{3+} redox couple is not utilized as the energy-bearing active materials. Although it often plays an important role in the balancing step of VRBs for bench-top flow cell tests, the VO^{2+}/V^{3+} redox reaction is often considered a self-discharge reaction after crossover [8,9]. As shown in Fig. 1, the reaction between $VO_2^+/VO^{2+}$and VO^{2+}/V^{3+} couples is favourable thermodynamically, with a theoretical cell voltage of 0.66 V. This reaction can be coupled with the reaction in conventional VRBs to produce a VRB, namely V4RB, which utilizes the same parent active species (VO^{2+}) on both sides of the flow battery. With a catholyte:anolyte volume ratio of 2:1, VO^{2+} is converted to VO_2^+ and V^{2+} at positive and negative sides, respectively. Such designs will further expand the merits of VRBs by improving the utilization of vanadium ions, and hence enhancing the theoretical volumetric capacity. Furthermore, the employment of the same parent active materials (i.e. V(IV)) could alleviate the crossover concerns at the discharged state, and potentially simplify the rebalancing step as well [10].

The feasibility of V4RBs was first demonstrated with an electrolyte composition of 2 M $VOSO_4$ in 5 M HCl solutions (denoted as V225), and a catholyte:anolyte volume ratio of 2:1. At a current density of 50 mA/cm^2, two major sets of charge/discharge plateaus were observed from voltage profiles of the flow cell (Fig. 2a). These two sets presumably correspond to the two-step reactions of the VO_2^+/VO^{2+}couple vs $VO^{2+}/V^{3+}$and V^{3+}/V^{2+} couples, as shown in Fig. 1.

As for the cycling performance, the round-trip coulombic efficiency (CE) was around 97%, while the energy efficiency (EE) was only around 35% at a current density of 50 mA/cm^2 (Figure S1 in the Supporting Information). This low energy efficiency is due to the high over-potentials during Step 1, as indicated by

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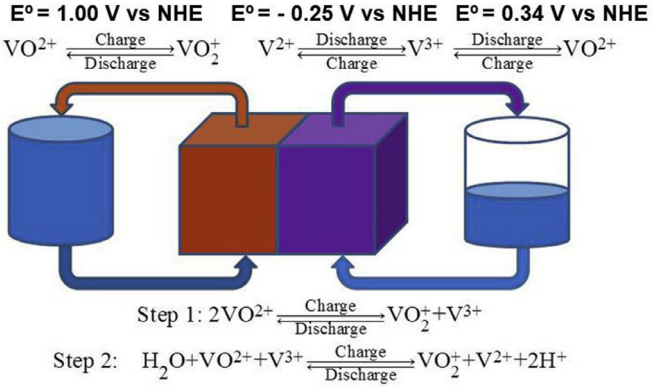

Fig. 1. Schematic figure for the design of all-vanadium (IV) flow batteries, or V4RB, with the same parent active species (VO^{2+}).

the large gaps between charging and discharging plateaus in Fig. 2a. Polarizations in VRBs are mostly attributed to Ohmic loss, mass transfer resistance, and charge transfer barrier [11]. With similar environments, Step 1 and 2 shared comparable Ohmic and concentration polarizations. Therefore, their substantial variations in over-potentials originate from intrinsic differences in kinetics of VO^{2+}/V^{3+} and V^{3+}/V^{2+} couples at electrode surfaces. In fact, previous voltammetry studies suggest that the VO^{2+}/V^{3+} couple demands a large activation energy during electrochemical reactions [8]. By decreasing the over-potential with a lower current density (20 mA/cm^2), EE can be promoted to around 50%. It is interesting to notice that a third discharge plateau was observed in the voltage profile at 20 mA/cm^2 (Figure S2 in the Supporting Information), indicating a possibly more complex process.

To enhance the performance of this V4RB system demands improvements on the kinetics of charge transfer processes in Step 1, especially the VO^{2+}/V^{3+} couple. Inspired by the fact that bismuth [11] and copper [12] nanoparticles are effective catalysts in conventional VRBs towards the V^{3+}/V^{2+} couple, two metal salts in the form of $BiCl_3$ and $CuCl_2$ were sequentially added to the anolyte side of the above flow cell system to test their effects on cell performances. Voltage profiles after the addition of Bi and Cu ions are illustrated in Fig. 2b and 2c. The introduction of these ions led to a slight decline of CE, but nevertheless promoted VEs and EEs (Figure S1 in the Supporting Information), although by a different margin. Specifically, compared with Bi ions, Cu ions are more effective in boosting the performance of this V4RB, and EEs rose to above 70% with their presence. Indeed, as shown in Fig. 2b and Figure S3 in the Supporting Information, the addition of Bi ions has minimal effect on the voltage curves of Step 1 (i.e. conversions related to the VO^{2+}/V^{3+} couple). The first charging plateau was lowered by a small margin (around 0.04 to 0.05 V), while the second discharging plateau almost overlapped with that of pristine electrolytes (V225). This suggests that deposited Bi metals during charging, instead of Bi ions, might be contributing. The mechanism might be by either lowering Ohmic losses through better electrode conductivities, or suppressing charge transfer polarizations through possible catalytic effects towards the VO^{2+}/V^{3+} couple. In comparison, Cu ions drastically altered the voltage profiles of Step 1, and significantly reduced the over-potentials. Two distinct charging plateaus were observed for Step 1 (Fig. 2c and Figure S3 in the Supporting Information), and compared with that before Cu addition, the first plateau was about 0.5 to 0.6 V lower, while the second one was on a similar voltage level. The two charging plateaus, however,

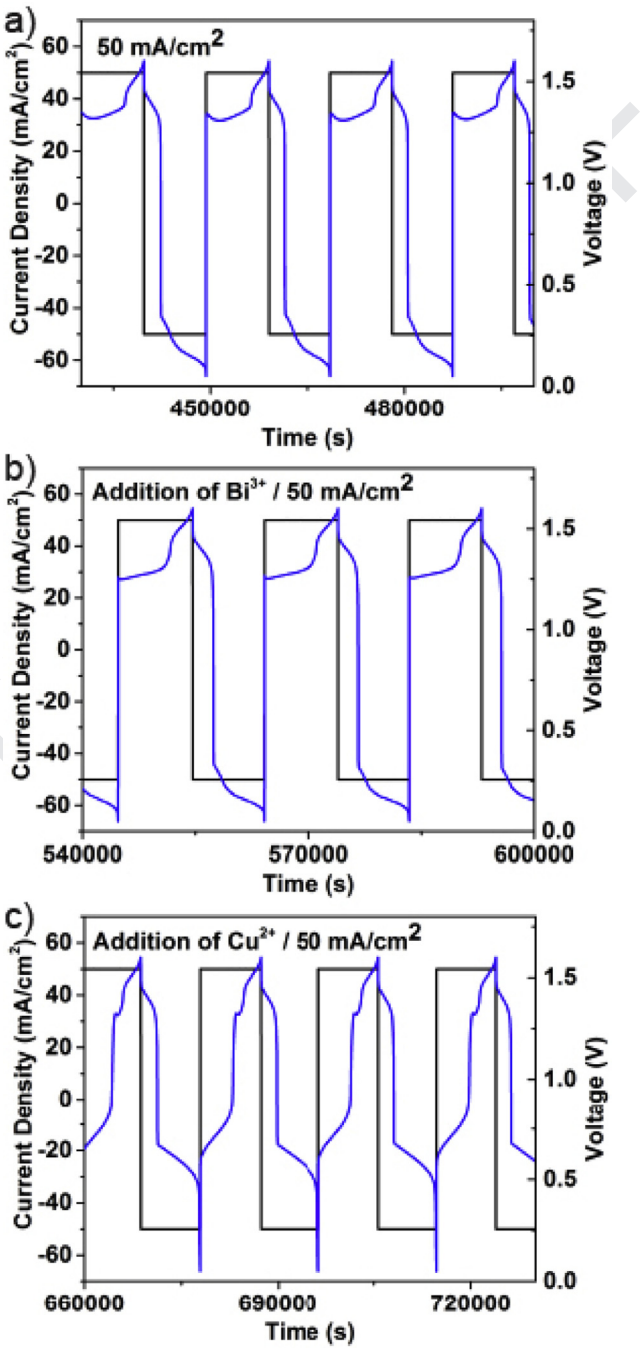

Fig. 2. Voltage profiles of the V4RB at a current density of 50 mA/cm^2 before and after the addition of metal salts: a: before salt additions, b: after the addition of 0.2 mmol $BiCl_3$ (apparent concentration: 10 mM) to the anolyte side, and c: after further addition of 0.2 mmol $CuCl_2$ (apparent concentration: 10 mM) to the anolyte side.

correspond to only one discharging plateau, which was increased by about 0.4 V after the addition of Cu. Such phenomena suggest that Cu ions or their derivative species during cycling only function within a certain SOC range during charging of Step 1. In the electrochemical processes during cycling, cyclic voltammetry (CV) results of the V225 electrolyte with 10 mM $BiCl_3$ and 10 mM $CuCl_2$ reveal a pair of peaks near 0.3 V vs. AgCl/Ag (Fig. 3a). This pair of peaks is around 0.6 to 0.7 V lower than that of the VO_2^+/VO^{2+}

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