An Electrolyte-Tank Switching Effect for Recycling Waste Electrolytes of a Vanadium Redox Flow Battery

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Introduction

- Vanadium redox flow batteries (VRFBs) are promising for grid-scale energy storage, but long-term operation leads to gradual capacity fade caused by vanadium crossover and side reactions [1]. Various recovery strategies have been reported, such as electrolyte remixing and chemical or electrochemical regeneration, each addressing specific aspects of electrolyte imbalance [2]. Continued exploration of such options is valuable, particularly for spent electrolyte generated by large-scale VRFB operation.
- Here we report on the capacity recovery of the spent electrolyte retrieved from a 100 kW/1 MWh-class VRFB demonstration system after long-term field operation. After cycling in a laboratory cell, the catholyte and anolyte roles were exchanged between the two tanks by reversing the cell polarity, without any additional treatment. Cycling was then continued, and the discharge capacity and electrolyte composition at the endpoint were examined before and after switching.

Results and Discussion

Table 1. Vanadium concentration and average oxidation state in Tank A and Tank B at three cycling stages.

Stage	Tank A	Tank B
Initial loading	1.717 M $V^{3.597+}$	
After pre-switch 250 cycles	1.525 M $V^{4.068+}$ (catholyte)	1.836 M $V^{3.493+}$ (anolyte)
After post-switch 200 cycles	1.722 M $V^{3.044+}$ (anolyte)	0.948 M $V^{4.072+}$ (catholyte)

- The spent electrolyte (1.717 M total vanadium, $V^{3.597+}$) was loaded into both tanks and cycled at 80 mA cm^{-2} with charge and discharge cut-off voltages of 1.65 and 0.7 V, respectively. Over the 250 pre-switch cycles, the average Coulombic, voltaic, and energy efficiencies (CE, VE, EE) were 96.85, 64.36, and 62.32%, respectively (Fig. 1a). The discharge capacity showed an overall decrease from 326 mAh in the first cycle to 12 mAh by the 250th (Fig. 1b). The CE remained high, indicating that little charge was lost to side reactions, while the lower VE and the widening gap between the charge and discharge profiles (Fig. 1c) point to increasing cell polarisation as the main source of the per-cycle efficiency loss.
- At the pre-switch endpoint, the two electrolytes reached clearly different states (Table 1). The anolyte in Tank B contained 1.836 M vanadium while the catholyte in Tank A contained 1.525 M, and the anolyte deviated further from its expected fully discharged oxidation state of $V^{3.0+}$ to $V^{3.493+}$.
- After switching, the average CE, VE, and EE were 97.45, 67.44, and 65.71%, respectively (Fig. 1d), and the discharge capacity recovered to about 196 mAh in the early post-switch cycles (Fig. 1e). The capacity then remained relatively stable through the 73rd cycle, after which it dropped abruptly from 239 to 153 mAh in a single cycle, with CE maintained, before declining to about 30 mAh by the 200th cycle.
- At the post-switch endpoint (Table 1), Tank A functioned as the anolyte and Tank B as the catholyte. Both were close to their expected fully discharged states, with Tank A at $V^{3.044+}$ (compared with $V^{3.0+}$ for a fully discharged anolyte) and Tank B at $V^{4.072+}$ (compared with $V^{4.0+}$ for a fully discharged catholyte), indicating that the oxidation-state imbalance was largely resolved. A difference in vanadium concentration, however, remained between Tank A (1.722 M) and Tank B (0.948 M), more pronounced than at the pre-switch endpoint.

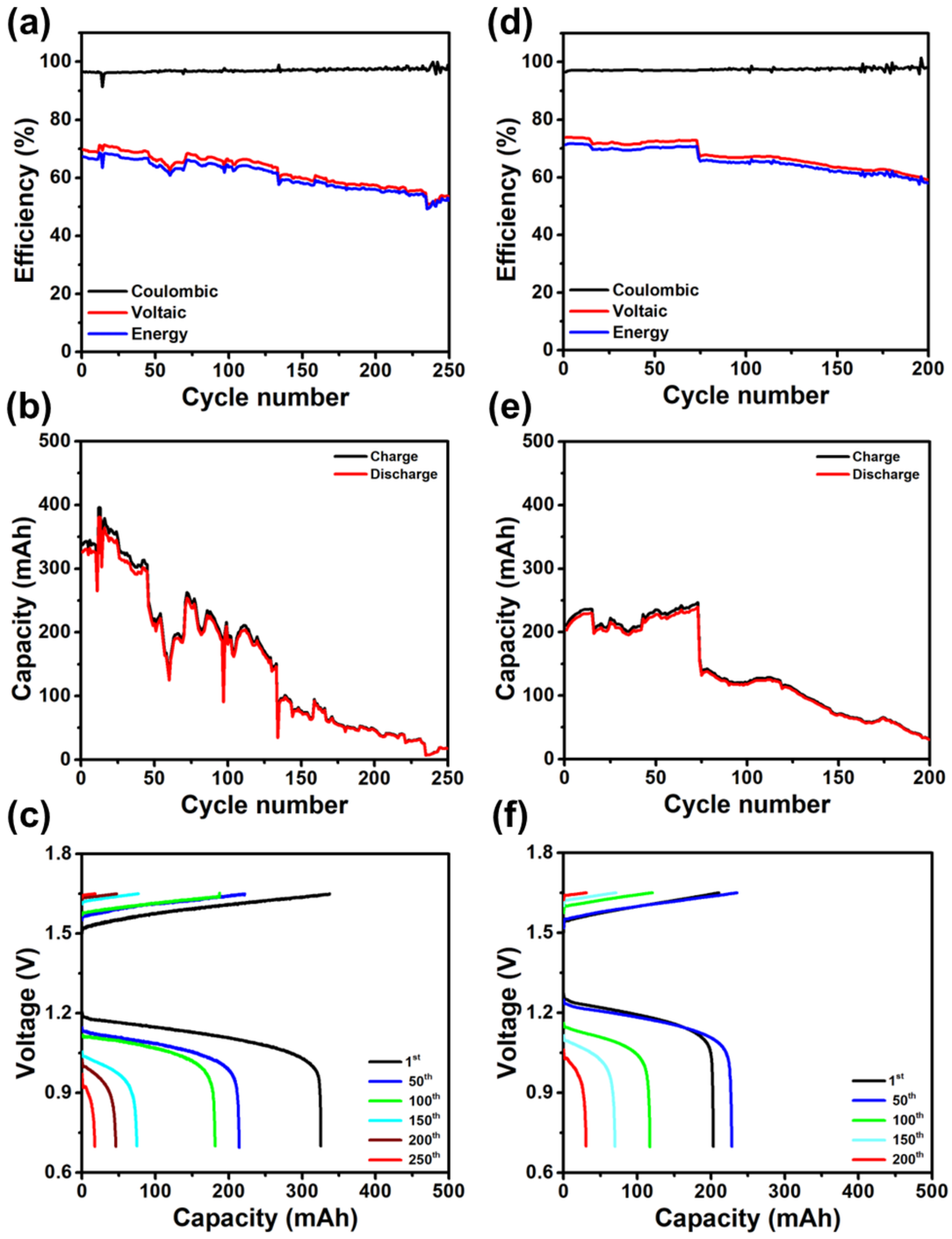

Fig 1. Cycling performance of the spent vanadium electrolyte before and after tank switching at 80 mA cm^{-2}: (a, d) efficiencies, (b, e) charge and discharge capacities, and (c, f) voltage profiles at the 1st, 50th, 100th, 150th, 200th (and 250th for pre-switch) cycles. (a–c) pre-switch 250 cycles; (d–f) post-switch 200 cycles.

Conclusion

- Spent vanadium electrolyte from a 100 kW/1 MWh-class VRFB demonstration system lost most of its accessible capacity over the 250 cycles (326 to 12 mAh). A simple electrolyte-tank switch, achieved by reversing the cell polarity with no chemical or electrochemical treatment, recovered the capacity to about 196 mAh, which was largely retained through the 73rd cycle before declining gradually thereafter. At the post-switch endpoint, the oxidation-state imbalance was largely resolved, whereas a difference in vanadium concentration remained between the two tanks. Electrolyte-tank switching therefore offers a practical option for the reuse of spent vanadium electrolytes, while the long-term behaviour after switching warrants further investigation.

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