

Development of XAFS Cell for Redox Flow Battery

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Redox flow batteries (RFBs) are attracting much attention as a stationary storage battery because of the safety operation and the easy recycling of active materials. However, the energy density is lower than that of lithium ion battery, and its improvement is a serious problem for the practical utilization of RFBs. For that purpose, it is essential to understand the mechanism of the charge and discharge reactions proceeded in RFBs. In this study, an *in-situ* XAFS cell to analyze the electrode reaction in RFBs has been developed and applied to observe the chemical state of the vanadium species in the $\text{VO}_2^+/\text{VO}^{2+}$ vs. $\text{V}^{3+}/\text{V}^{2+}$ RFB system.

A schematic draw of the developed XAFS cell for RFBs is shown in Fig. 1. A sheet of Nafion[®] membrane separates two carbon papers ($24 \times 17 \text{ mm}^2$), which work as the electrodes, and they soak the acidic aqueous solutions of $\text{VOSO}_4 \cdot n\text{H}_2\text{O}$ ($n = 4.2$) or VCl_3 dissolved in 3.0 M H_2SO_4 . These parts are sealed using two PEEK plates with rubber gaskets. The electric current is collected by a gold wire, which penetrates the PEEK plate to contact with the carbon electrode. Two electrodes are placed with the overlap area of 2 mm width.

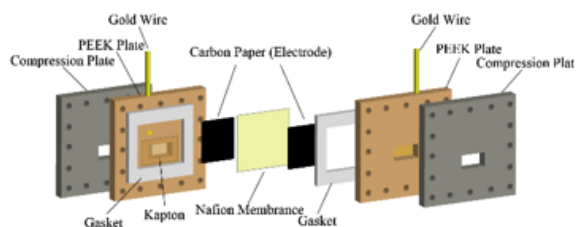


Fig. 1 Components of the developed XAFS cell for RFBs.

Two-dimensional XAFS imaging measurements were carried out at the vanadium K edge at BL-4 of the SR center (Ritsumeikan) and BL-7C of the Photon Factory (KEK) during the charge/discharge processes under the constant current condition.

The charge and discharge curves of the RFB are shown in Fig. 2. The XAFS imaging measurements were carried out at the 9 points during the charge/discharge cycle indicated in Fig. 2. The curve for the charge process showed a plateau at 1.4–1.6 V, and the capacity was 2.0 mA h. It is equivalent to the value expected from the amount of the vanadium species soaked in the carbon electrode. The charge reaction has progressed quantitatively using the developed *in-situ* XAFS cell. In the discharge process, the voltage plateau was observed at 1.2–1.5

V, and the discharge capacity was 1.6 mA h, which was *ca.* 80% of the charge capacity. The observed XANES spectra are shown in Fig. 3. The spectra clearly showed the reversible redox reactions for the $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ couples, indicating the successful development of the *in-situ* XAFS cell for RFBs.

References

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- (2) L. Wu, J. Wang, Y. Shen, L. Liu, and J. Xi, *Phys. Chem. Chem. Phys.*, **2017**, *19*, 14708.

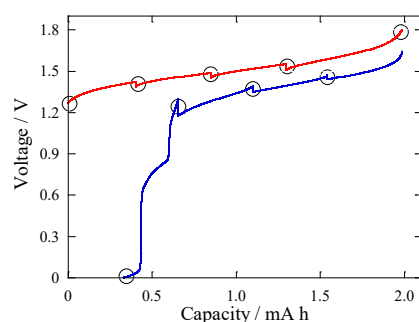


Fig. 2 Charge (red) and discharge (blue) curves operated using the developed *in-situ* XAFS cell for RFBs. The XAFS measurements were carried out at the points indicated by circles.

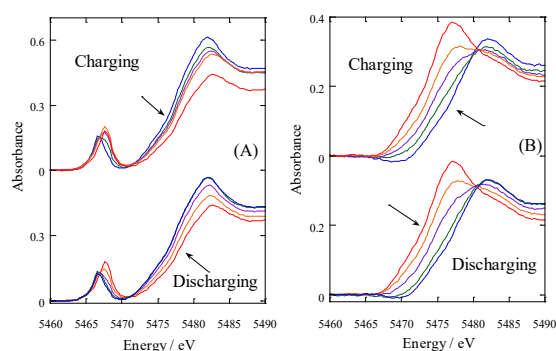


Fig. 3 XANES spectra of V species on the positive electrode side (A) and the negative electrode side (B) during the charge and discharge process.