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In Situ Chemical Techniques to Adjust the State-of-Charge of Vanadium Redox Flow Battery Electrolytes

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Flow batteries differ from other types of battery in that the electroactive materials are wholly (as is the case with the vanadium redox battery) or partly (as with the Zn-Br battery) dissolved in the electrolyte. The electrodes act as an inert surface on which the electrochemical reactions may take place. Because the electroactive components are not an integral part of the electrode structure flow batteries have several advantages over conventional types:

1) The power and energy of the battery may be independently selected
2) The cycle lives are typically very high
3) Additional capacity can be added by adding more electrolyte
4) The weight of the battery can easily be distributed in different ways, by choosing different tank designs
5) There is no memory effect

The vanadium redox flow battery was suggested by Thaller [1] and Pelligri and Spaziante [2] and, in its present form, by Skyllas-Kazacos [3].

The vanadium redox battery (VRB) consists of a stack of flow cells, which are internally divided by an ion-exchange membrane. Positive electrolyte containing a mixture of $(VO_2)_2SO_4$ and $VOSO_4$ in H_2SO_4 is pumped through one side of the cells and negative electrolyte containing a mixture of VSO_4 and $V_2(SO_4)_3$ through the other. The electrolytes are continuously circulated through the cells to separate storage tanks and back.

Carbon felt electrodes are used one both sides of the cells to provide a high surface area interface with the electrolytes. In addition appropriate carbons have a high stability in both reducing and oxidizing acidic environments.

During the process of charge and discharge the overall cell reaction is:

$$VO^{2+} + V^{3+} + H_2O = VO_2^{+} + V^{2+} + 2H^{+}$$

From which it may be seen that the same total amount of vanadium should be present in both electrolytes, in order for optimum usage. Additionally the state-of-charge (SOC) of both electrolytes, defined as the ratio of amounts of charged species to discharged species (i.e. V(V) to V(IV) or V(II) to V(III)), must also remain constant.

However, the equilibrium may be disturbed by asymmetrical parasitic reactions such as evolution of hydrogen at the negative electrode:

$$2VO^{2+} + 2H_2O = 2VO_2^{+} + 2H^{+} + H_2$$

If the system becomes slightly unbalanced in the SOC of the electrolytes there can be a significant loss of available capacity.

This is a problem common to many redox flow batteries and has been solved in the past by the use of additional rebalancing cells. These add cost and complexity to the system and must be maintained appropriately. In an effort to avoid the need for electrochemical rebalancing cells *in situ* chemical techniques have been examined.

The approach to stack construction adopted here was to connect monopolar cells by external electrical connections in order to provide a higher voltage cell stack. The external connections allowed independent monitoring of cell potentials and relatively easy replacement of cells if required. They could also be used theoretically with suitable switching components to adjust the stack potential to change from parallel to serial arrangements.

Additionally measurements were made on individual cells.

The effect of various chemical rebalancing strategies are examined in this work, in terms of cost, convenience, efficacy and performance of the VRB.

References

1. L. H. Thaller, in US Patent **3996064** (1975), *to NASA*
2. A. Pelligri and P. M. Spaziante, in GB Patent **2030349** (1978), *to Oronzio de Nori Impianti Elettrochimici S.p.A.*
3. M. Skyllas-Kazacos, in AU Patent **575247** (1986), *to Unisearch Ltd.*