Vanadium/Water Electrolyser to Recharge Vanadium/Oxygen Flow Batteries and Rebalance Vanadium-Redox-Flow-Batteries

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The vanadium/oxygen fuel cell (VOFC) has evolved from developments to vanadium redox flow batteries (VRFB) for storage of renewable energy and perhaps for mobile applications. In VOFCs, oxygen is used to oxidise divalent vanadium ions to trivalent ions instead of the redox reactions of V(IV)/V(V) to achieve potentially higher energy densities and eliminate temperature stability problems associated with the energy storage medium compared to VRFBs. To charge a VOFC as an energy storage system, the discharge reactions have to be reversed with as few side reactions as possible. This process involves reducing trivalent vanadium ions to divalent vanadium ions through the application of electrical energy. The cathodic water generated during the discharge is used as the reductant. The water itself is oxidised to oxygen to keep the cycle between the charge and discharge processes as short and efficient as possible:

Pos. El.:
$$2 \text{ H}_2\text{O} \rightleftharpoons \text{O}_2 + 4 \text{ H}^+ + 4 \text{ e}^ \varphi_A^0 = +1.23 \text{ V}$$

Neg. El.: $\varphi_C^0 = -0.255 \text{ V}$
Cell: $4 \text{ V}^{3+} + 2 \text{ H}_2\text{O} \rightleftharpoons \text{O}_2 + 4 \text{ V}^{2+} + 4 \text{ H}^+$ $\varphi_Z = 1.49 \text{ V}$

This process is also exactly the reversal of the process which happens in VRFBs when atmospheric oxygen oxidizes divalent vanadium ions in vanadium electrolytes. As a synergistic effect, vanadium/water electrolysis can be also used to regenerate oxidized electrolytes and increase the life time of the batteries.

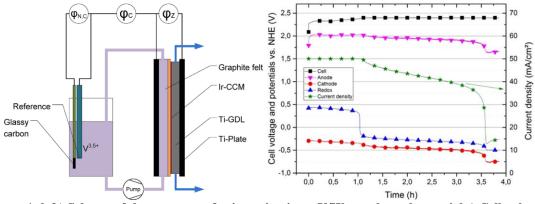


Figure 1: left) Scheme of the test set-up for investigating a V/Water electrolyser, right) Cell voltage, potentials and current density of a vanadium/water electrolyser (1.6 M V^{3,5+}, 2 M H₂SO₄, 40 cm²). Using a cell with a commercial and iridium-based catalyst coated membrane, it was possible to fully reduce V^{3,5+} and V³⁺ solutions to V²⁺ with the formation of oxygen and with coulomb efficiencies of over 96%. The process was followed by introduction of an additional reference electrode to measure the redox potential of the electrolyte, the negative electrode potential and to calculate the positive redox potential. The cell achieved a maximum current density of 75 mA/cm² during this process and was limited by the proximity of the V(III) reduction to the hydrogen evolution reaction. Due to the specific reaction mechanisms of V(IV) and V(III) ions, V(III) solutions were reduced with an energy efficiency of 61%, making this process nearly twice as energy efficient as the reduction of V(IV) to V(III). Polarisation curves and electrochemical impedance spectroscopy were used to further investigate the losses of half-

cell reactions and to find ways of further increasing efficiency and performance levels.