New electrode materials for the positive electrolyte of the all vanadium redox flow battery.

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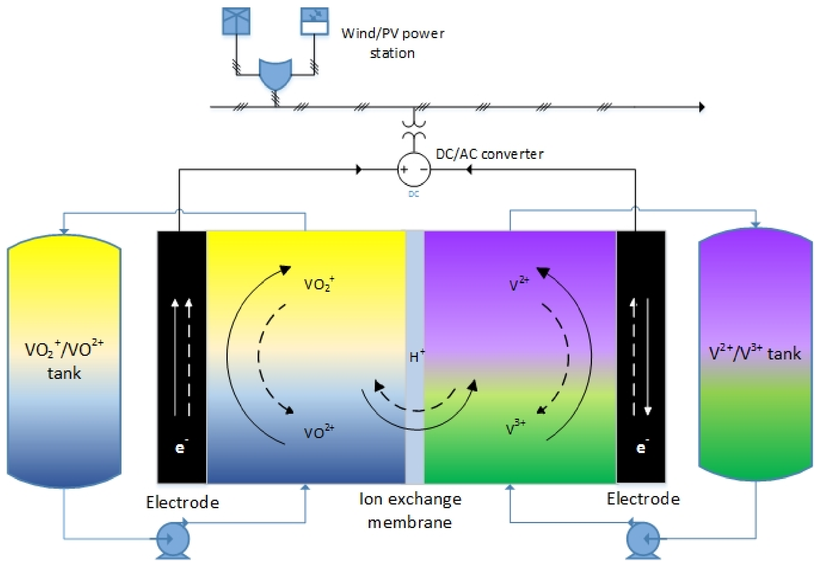
REDOX flow battery

Regenesys polysulfide bromide RFB, Little Barford, UK

Advantages of REDOX Flow Batteries [1,2]

- Energy stored for long periods of time
- Wide range of storage capacities
- The power conversion is separated from the energy storage
- The same cell allows the conversion from electric to chemical energy and vice versa
- It can be fully discharged and left uncharged for long periods of time
- Electrolyte can be replenished
- Modularity
- Transportable at any state of charge

All-vanadium redox flow battery VRFB



$$VO^{2+} + H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} VO_2^+ + 2H^+ + e^- \quad E° = 1.0 \text{ V } \textit{vs.} \text{ SHE}$$

$E°_{cell}$ = 1.26 V *vs.* SHE

$$V^{3+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} V^{2+} \quad E° = -0.26 \text{ V } \textit{vs.} \text{ SHE}$$

Challenges with the V(V)/V(IV) electrolyte

- Low solubility of V_2O_5
- Thermal precipitation of V(V) at temperatures above 40ºC
- **Dissolution, wear of carbon electrodes**
- Comparison of the potentials of OER with V(IV) → V(V)

Aim

Test different electrode materials that are used in other electrochemical applications, have a high OER overpotential that does not interfere with the oxidation potential of the vanadium electroactive species and undergo similar operation conditions showing a long service lifetime. A special interest is given to the dimensional stable anodes (DSA), developed since the early 70's [3], and that have been used broadly in the chlor-alkali industry and for water treatment.

Alongside the DSA, boron doped diamond (BDD), gold and platinum electrodes will be tested to compare their performance and electrochemical behaviour and determine the characteristics of the vanadium redox reactions.

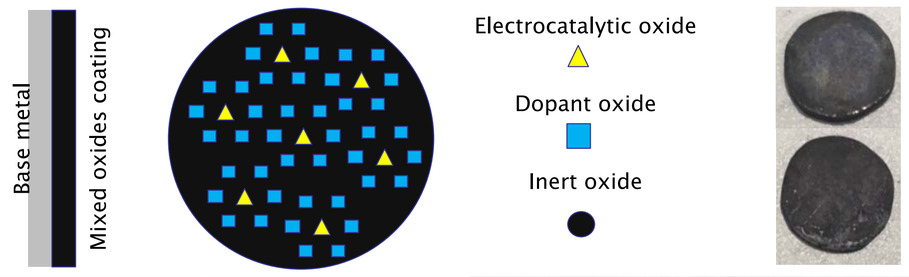
Objectives

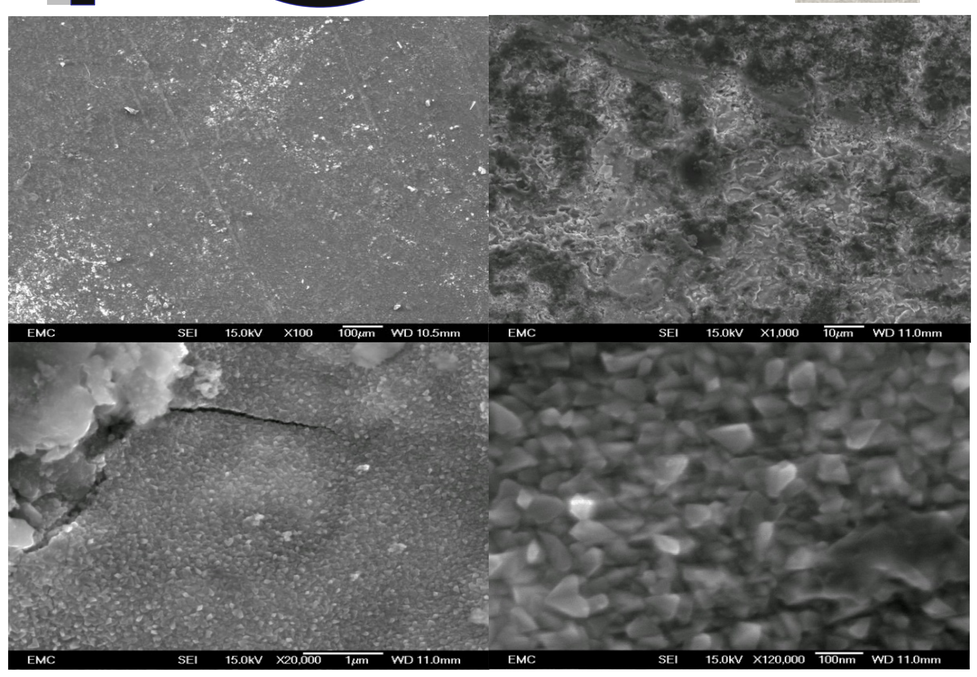
• Determine the behaviour of gold, platinum and BDD electrodes in an electrolyte containing V2O5 dissolved in sulphuric acid

• Determine a good composition of DSAs based in a thoroughly literature review and experiments with electrodes manufactured in the laboratory

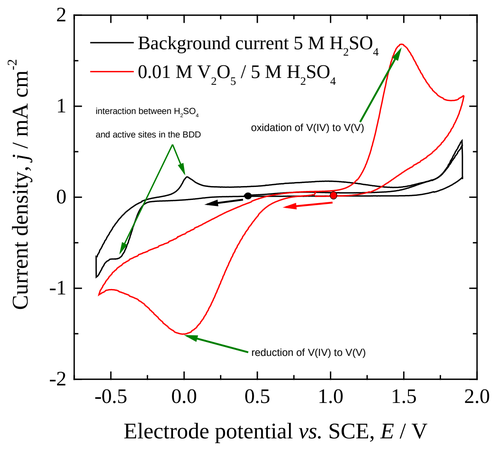
Dimensional stable anode

The main configuration of a DSA can be described as Me/AOx-BOy [4], where Me is the base metal, AOx is the electrocatalytic oxide and BOy is the inert protective oxide. Dopants can be added to the coating to increase the conductivity.

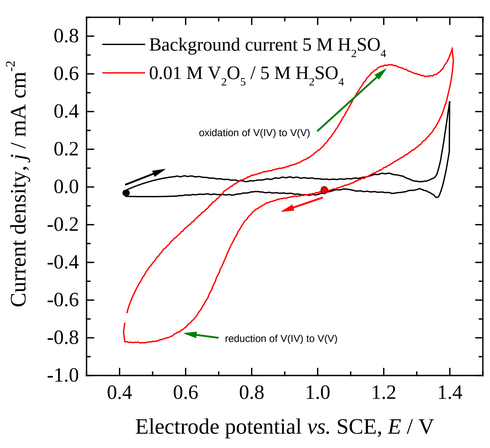




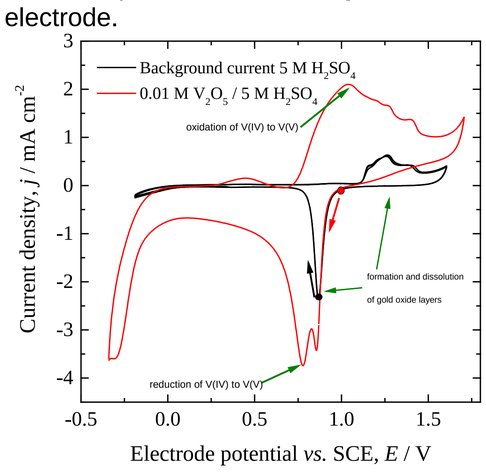
Different electrode materials for the VO_2^+/VO^{2+} electrolyte



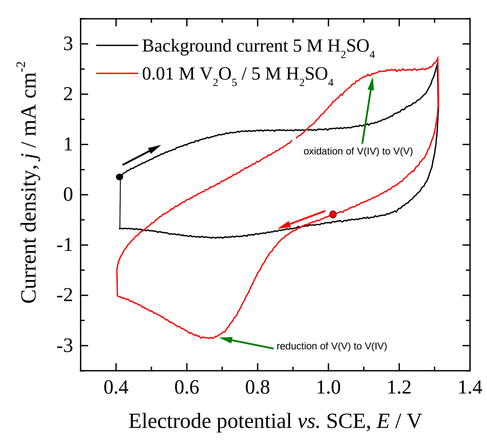
Cyclic voltammograms for the VO_2^+/VO^{2+} redox couple at the **boron doped diamond** electrode.



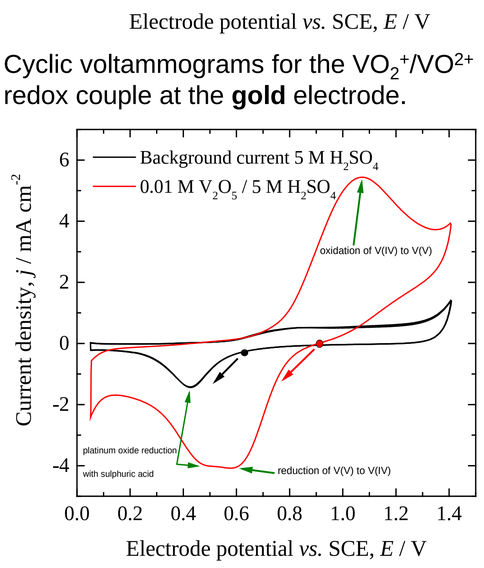
Cyclic voltammograms for the VO_2^+/VO^{2+} redox couple at the **DSA 1 (49.66% IrO_2, 49.66% SnO_2, 0.68% Sb_2O_5)** electrode.



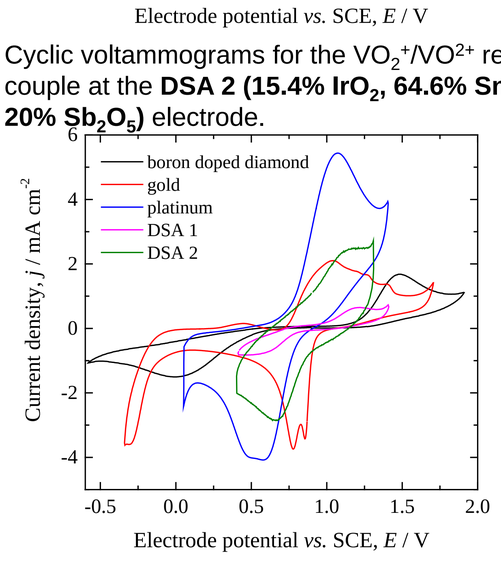
Cyclic voltammograms for the VO_2^+/VO^{2+} redox couple at the **gold** electrode.



Cyclic voltammograms for the VO_2^+/VO^{2+} redox couple at the **DSA 2 (15.4% IrO_2, 64.6% SnO_2, 20% Sb_2O_5)** electrode.



Cyclic voltammograms for the VO_2^+/VO^{2+} redox couple at the **platinum** electrode.



Electrode material CV comparison

Conclusions

- The BDD electrode showed well defined and show linear behaviour with changing scan rates in the cyclic voltammetries. Nevertheless, the big current peak potential separation shows a non-reversible behaviour and it cannot be used as an electrode for the positive electrolyte of the VRFB.
- The gold electrode has a huge interaction with sulphuric acids due to the dissolution and deposition of gold oxides on its surface and represented as a series of peaks. The current peaks related to the oxidation and reduction of the vanadium are located in the vicinity of these potentials, making it not a good option for use it as electrode in the VRFB.
- The platinum electrode shows a reduction reaction of the platinum oxides with the background solution in the form of a reduction peak located close to the reduction of V(V) to V(IV). This diminishes the performance efficiency of the electrode due to the current lost in this undesired reduction peak. Platinum can be discarded as an active electrode material for the VRFB due to its poor performance and high price.
- The dimensional stable anodes showed no interaction with the background solutions, unlike all the previous materials tested. Different composition of the oxide layer in the DSA showed great improvement in the performance. When the iridium oxide proportion was decreased (from almost 50 % to 15 %), this lead to a huge increment in the current density, being more than three times higher than with the high iridium content electrode. Also the potential between the redox peak currents was diminished, showing a better quasi-reversible behaviour.
- The DSA is a promising material if the reversibility can be improved as well as the conductivity of the electrode.

Further work

• The effect of the electrode geometry for DSA

• Further improvement of the oxide coating of the DSA

References

[1] C. Ponce de León, A. Frías-Ferrer, J. González-García, D. A. Szánto, and F. C. Walsh, "Redox flow cells for energy conversion," *Journal of Power Sources,* vol. 160, pp. 716-732, 9/29/ 2006.

[2] P. Leung, X. Li, C. Ponce de León, L. Berlouis, C. T. J. Low, and F. C. Walsh, "Progress in redox flow batteries, remaining challenges and their applications in energy storage," RSC Advances, vol. 2, p. 10125, 2012.

[3] H. B. Beer, "Electrode and coating therefor," United States of America Patent 3,632,498, 1972.

[4] C. Comninellis and G. P. Vercesi, "Problems in DSA coating deposition by thermal decomposition," *Journal of Applied Electrochemistry,* vol. 21, pp. 136-142, 02/01/Number 2/February 1991 1991.