

Electrolyte imbalance determination of a vanadium redox flow battery by potential-step analysis

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Introduction

Vanadium redox flow batteries (VRFB) suffer from capacity fades due to side reactions and crossover effects through the membrane. Side reactions lead to a deviation of the optimal initial average oxidation state (AOS = +3.5) of vanadium species in both half-cell electrolytes. In order to rebalance the electrolyte solutions, it is first necessary to determine the current AOS.

Different methods for analyzing the AOS in VRFBs have been presented in the literature, such as potentiometric titration of the oxidation state of the two electrolytes or of the mixed electrolytes, analysis of the UV/Vis absorption spectra or using special cells allowing to monitor and analyze the half-cell potentials of the electrolytes versus a reference electrolyte. [1-7] All methods have individual drawbacks, e.g. the disadvantages of ex situ analysis, the need of special equipment and/or time-consuming procedures.

We developed a new method to determine the AOS of mixed electrolytes by using a standard OCV cell. [8]

Experimental

Please refer to [8] for experimental details.

Results and discussion

For a proper analysis, both half cells need to have the same amount of substances of vanadium species, e.g. the same volumes of pre-mixed electrolytes (i.e. the electrolytes have the same concentration of vanadium species). If the AOS of the electrolytes is $AOS \neq +3.5$, a potential step in the OCV during constant current initial charging of the electrolytes can be observed (schematically depicted in Fig. 1).

If the $AOS > 3.5$ (normally occurring during operation), the AOS can be determined by analysing the potential step using the following equation:

$$AOS = \frac{4t_{V4+} + 3t_{V3+}}{t_{V4+} + t_{V3+}}$$

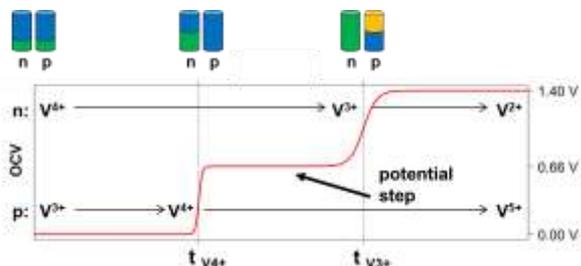


Figure 1 Schematic of the potential step occurring during the first charging of mixed electrolytes with $AOS \neq 3.5$ (n = negative electrolyte, p = positive electrolyte) [8].

The method was validated using electrolytes with defined AOS obtained by mixing appropriate amounts of vanadium electrolytes with $AOS = +3$ and $AOS = +4$ (= electrolytes from a fully discharged VFB). The potential steps in OCV during charging of equal amounts of electrolytes with the pre-defined AOS and the first derivative are shown in Fig. 2. It is necessary to determine the time interval of the potential step. It can be seen that the first derivative is well suited to precisely determine the begin and the end point of the potential step.

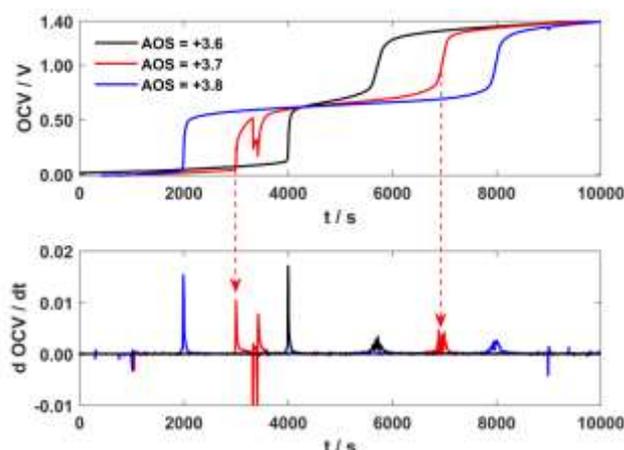


Figure 2 Potential steps during charging of electrolytes with prepared AOS of 3.6, 3.7 and 3.8 in both tanks [8].

The method was also applied to a real vanadium redox flow battery system during cycling (Fig. 3). As expected, the potential step increases during cycling which indicates an ongoing increase of the AOS during cycling (assumed to be caused

by hydrogen evolution and/or the impact of oxygen from the air).

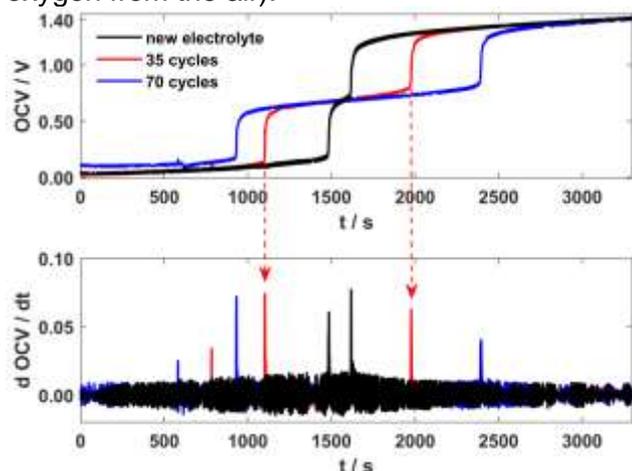


Figure 3 Potential steps during charging of mixed electrolytes used in a VFB system before cycling and after 35 and 70 cycles [8].

The Errors in imbalance detection are shown in Tab. 1. The errors are well competitive in comparison to other techniques (5% for potentiometric titration [3] and 7.8% for the UV/Vis detector [4]).

Conclusion

This method of determination of the AOS is simple, accurate, straightforward. For real life application it is advantageous that no additional equipment is needed and that the method is non-invasive.

Electrolyte sample	AOS potential step	AOS UV/Vis	Δ AOS	Error in imbalance detection
a) AOS = 3.5 prepared	+3.487	-	0.013	2.6 %
AOS = 3.6 prepared	+3.588	-	0.012	2.4 %
AOS = 3.7 prepared	+3.697	-	0.003	0.6 %
AOS = 3.8 prepared	+3.800	-	0	0 %
b) „New“ electrolyte	+3.469	+3.497	0.028	5.6 %
After 35 cycles	+3.644	+3.624	0.020	4.0 %
After 70 cycles	+3.720	+3.691	0.029	5.8 %

Table 1 Comparison of AOS determined by the potential-step analysis with a) the prepared AOS and b) the AOS determined by UV/Vis analysis [8].

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