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Short communication

Detection of capacity imbalance in vanadium electrolyte and its electrochemical regeneration for all-vanadium redox-flow batteries

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HIGHLIGHTS

- UV–vis detection of V(III) fraction all-vanadium redox-flow battery electrolyte.
- Isosbestic point at 600 nm as a reference point for common electrolyte batches.
- Rebalancing procedure based on pre-charging and remixing.

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ABSTRACT

A vanadium electrolyte for redox-flow batteries (VRFB) with different V^{III} and V^{IV} mole fractions has been studied by UV–vis spectroscopy. Spectrophotometric detection enables a rough estimate of the V^{IV} and V^{III} content, which can be used to detect an electrolyte capacity imbalance, i.e. a deviation in the mole fraction of V^{IV} or V^{III} away from 50%. The isosbestic point at 600 nm can be used as a reference point in the analysis of common VRFB electrolyte batches. The VRFB electrolyte is observed to have an imbalance after prolonged storage (a couple of years) in a tank under ambient conditions. A regeneration procedure, which involves pre-charging the unbalanced electrolyte and mixing part of it with a portion of initial unbalanced electrolyte, has been tested. The resulting rebalanced electrolyte has been compared with a common electrolyte in a charge–discharge cell test and is shown to be suitable for cell operation.

1. Introduction

Vanadium salts dissolved in sulfuric acid are used for energy storage in all-vanadium redox-flow batteries (VRFBs) [1,2]. During battery discharge vanadium species undergo redox reactions of V^{V} to V^{IV} in the positive half-cell, and V^{II} to V^{III} in the negative half-cell. A mixture of V^{III} and V^{IV} species in a 50:50% mole ratio (referred to as $V^{3.5+}$ electrolyte) is often used as a commercially-available starting electrolyte for VRFBs, and needs to be charged to form V^{III} as an anolyte and V^{IV} as a catholyte for further battery operation.

During long-term performance the VRFB electrolyte is reported to become unbalanced [3–5]. Imbalance implies an inequality in the amount of oxidized and reduced species in a VRFB, and is usually caused either by vanadium cross-over through the membrane or by side reactions such as hydrogen evolution in the anolyte. It results in capacity losses, and 100% state-of-charge (SoC) can then be achieved only in one half-cell of the VRFB. To detect the imbalance, the oxidation state and the concentration of vanadium species can be determined and compared. A direct analysis can be performed based on the potentiometric titration of VRFB samples; however, this is time-consuming and unsuitable for continuous electrolyte monitoring or for monitoring online. Indirectly, the SoC can be estimated from its correlation with the electrolyte absorption in the visible range (although this is difficult to use in practice for the catholyte [6]) or from the correlation between the open circuit potential and the vanadium concentration. For the latter technique, a special reference cell is connected to the electrolyte circuit, and the electrical measurement set-up is adapted to it [4,5].

All the above mentioned approaches to detect vanadium electrolyte imbalance concern the analysis of the anolyte and catholyte, i.e. mixtures of V^{II}/V^{III} and V^{IV}/V^{V}. In this paper we report the imbalance of common $V^{3.5+}$ electrolyte, which is found to occur during its long-term storage before it is introduced into the battery.

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As a powerful VRFB system (for example 2 MW/20 MWh) requires several hundred m^3 of electrolyte, it is necessary to transport and store batches of electrolyte and to be able to monitor the consistency of their chemical properties over time before they are introduced into the battery. This electrolyte undergoes an alteration of V^{III} content during storage in a tank over a couple of years, and the ratio of V^{III} to V^{IV} consequently shifts. As vanadium electrolyte is an important factor in the total costs of the VRFB system, and the published literature on electrolyte rebalancing mostly considers the concentration shifts in the electrolyte during battery operation, we here present an approach for the rapid spectrophotometric identification of imbalance in common $V^{3.5+}$ electrolyte, and a procedure for the electrolyte pre-treatment to overcome the imbalance. The proposed pre-treatment is based on electrolysis and mixing of electrolyte portions to obtain separate V^{III} and V^{IV} electrolyte solutions.

2. Experimental

2.1. Chemicals and material

Vanadium electrolyte solution ($V^{3.5+}$) with a 50:50% mole fraction of V^{III} and V^{IV} at a total vanadium concentration of 1.55 M, 2 M sulfuric acid and approx. 0.05 M phosphoric acid (GfE Gesellschaft für Elektrometallurgie mbH, Germany) was used as a reference electrolyte, and to prepare samples with various V^{III}:V^{IV} ratios. Samples of the same $V^{3.5+}$ electrolyte which had been stored in a tank and exposed to ambient temperature fluctuations over a couple of years were used as an unbalanced electrolyte. The Fumasep FAP-450 membrane (FuMa-Tech GmbH, Germany) was used as the separator. GFA6 graphite felt (SGL Group, Germany) and FU 4369 graphite bipolar plates (Schunk Kohlenstofftechnik GmbH, Germany) were used as electrode current collector materials in a 40 cm^2 cell assembly for the charge–discharge test (for details of cell design, see Ref. [6]). The felts were pre-treated for one hour at 400 °C in the oven before the cell assembly, and were compressed by 10% of their thickness in the cell. The electrolyte flow rate was 75–80 ml/min. A 40 cm^2 cell of the same design was used for galvanostatic electrolysis to prepare the electrolyte samples with various V^{III}:V^{IV} ratios and for pre-charging (i.e. rebalancing) of the unbalanced electrolyte. The vanadium concentrations in all the electrolyte samples were determined by potentiometric titration.

2.2. UV–vis characterization

The absorbance of vanadium electrolyte samples was recorded with a Shimadzu 1650PC UV–vis double beam spectrophotometer. These measurements were carried out in matched quartz cuvettes with a 0.2 mm optical path length.

2.3. Electrochemical procedures

The charging of electrolyte for rebalancing was carried out galvanostatically at 20 mA cm^{-2} until the redox potential of the anolyte reached approx. 0.5 V vs. Hg/Hg_2SO_4 electrode. The redox potential of the anolyte was monitored using a glassy carbon electrode incorporated into the electrolyte circuit. The charge–discharge cell test was performed using a Basytec battery tester (Basytec GmbH, Germany) in galvanostatic mode: the end-of-charge voltage was set to 1.65 V and the end-of-discharge voltage was 0.8 V. Between the cycles the cell was kept at open circuit potential for five minutes. At each current density (from 25 mA cm^{-2} to 100 mA cm^{-2}) five cycles of charge–discharge were performed. Each charge–discharge measurement was repeated for reproducibility. The titration of electrolytes samples was carried out with 0.1 M cerium(IV) sulfate standard solution using Titrator T70 (Mettler Toledo Int. Inc., Germany).

3. Results and discussion

3.1. Visible spectroscopy characterization

To model the unbalanced electrolyte samples with different formal charges from 3+ to 4+ but a constant total vanadium concentration, the common $V^{3.5+}$ electrolyte was galvanostatically charged over a predefined time. These samples were studied using UV–vis spectroscopy. The absorbance spectra of these electrolyte solutions with different ratios of V^{III} to V^{IV} are shown in Fig. 1. The absorption spectrum of neat V^{III} has two characteristic peaks at 401 and 600 nm. The extinction coefficients of V^{III} estimated in the concentration range from 0.2 M to 1.6 M are 13.1 M^{-1} cm^{-1} at 401 nm and 7.5 M^{-1} cm^{-1} at 600 nm. The absorption spectrum of neat V^{IV} shows a band positioned at a maximum of 760 nm with a shoulder at 600 nm [7,8]. A linear dependence between the absorption at 760 nm and the V^{IV} concentration has been observed, at least in the range from 0.2 M to 1.6 M. The extinction coefficient of V^{IV} at 760 nm is 19.5 M^{-1} cm^{-1}. It can be seen that the spectra of mixtures consisting of V^{III} and V^{IV} are the convolution of V^{III} and V^{IV} absorptions. The evolution of spectra with an increase in the V^{IV} fraction results in the appearance of an isosbestic point, which is consistent with the fact that the common electrolyte is a mixture of non-interacting V^{III} and V^{IV} species and that the analytical concentration of vanadium is constant throughout the series [6]. All three characteristic peaks can be seen for the 50:50% mixture of V^{III} and V^{IV}. The unbalanced electrolyte displays a lower absorption at the isosbestic point (dashed line, Fig. 1), so the total vanadium concentration in this sample is lower. This is in good agreement with redox titration data: the total vanadium concentration is 1.4 M compared to an initial concentration of 1.55 M. It means that the slow oxidation of V^{III} by air cannot be the main reason for the shift in the V^{III}:V^{IV} ratio, and V^{III} is likely to precipitate out of the electrolyte solution.

To be used for quantitative analysis, V^{III} and V^{IV} bands, which are overlapped on the spectra of the mixtures (curves (2) to (10) in Fig. 1), should be deconvoluted, especially for V^{IV} fractions up to 40%. However, as can be seen in Fig. 2, the ratio of absorbance taken at 760 nm and at 401 nm (Abs_{760}/Abs_{401}) can be used to roughly detect an V^{III}:V^{IV} ratio shift. The dependence of Abs_{760}/Abs_{401} in

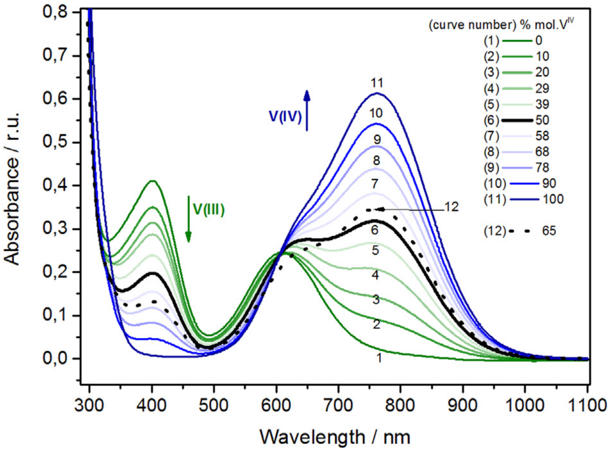

Fig. 1. Evolution of absorption spectra in the visible range for vanadium electrolyte as a function of the V^{IV} molar fraction. Total vanadium concentration is 1.55 M for samples (1)–(11), and 1.4 M for the sample (12).