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Monitoring the State of Charge of the Positive Electrolyte in a Vanadium Redox-Flow Battery with a Novel Amperometric Sensor

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Abstract: Vanadium redox-flow batteries are a promising energy storage technology due to their safety, long-term stability, and independent adjustability of power and capacity. However, the vanadium crossover through the membrane causes a self-discharge, which results in a capacity shift towards one half cell. This leads to a gradual decrease in its efficiency over time. Capacity balancing methods for compensation of this effect require a reliable online state of charge (SoC) monitoring. Most common methods cannot provide exact values of the individual concentration of each species in both electrolytes. In particular, the state of the positive electrolyte cannot yet be precisely determined. In this work, an amperometric SoC monitoring is proposed as a new approach. First, the suitability of the principle is investigated with a rotating disc electrode (RDE). Then, a sensor based on a gas diffusion layer (GDL) is developed and tested in the positive electrolyte. The dependencies between oxidative current and V(IV)-concentration are examined as well as those between reduction current and V(V)-concentration. Using both relationships, a reliable measurement of all relevant concentrations is possible.

Keywords: state of charge (SoC) monitoring; amperometric sensor; diffusion limitation; rotating disc electrode (RDE); gas diffusion layer (GDL)

1. Introduction

With the rising share of renewable energy sources, the demand for energy storage systems is also increasing. One promising technology to compensate for the fluctuation of solar and wind energy is the vanadium redox-flow battery (VFB). Flow batteries are characterized by individual adjustment of power and capacity through the separate design of cell size and electrolyte tank. The electrolyte is then pumped through the two half cells during operation. Vanadium is a very suitable active material for energy storage, as it can be present in four oxidation states and therefore can be used in both half cells. This minimizes the risk of permanent electrolyte deterioration by cross-contamination due to cross-over through the membrane. Nevertheless, cross-over processes are still a problem for the long-term operation of VFBs, as they lead to continuous self-discharge of the battery. In combination with side reactions (e.g., hydrogen evolution on the negative electrode [1]), this leads to concentration shifts of the individual vanadium concentrations in the tanks. During long-term cycling, this results in a decrease of the available capacity and therefore limits the depth of discharge (DoD) and the battery efficiency [2]. The capacity can be restored by various capacity balancing strategies, such as remixing or a continuous overflow [3]. To apply these balancing methods, it is absolutely necessary to know the exact condition of the battery. Therefore, a reliable state of charge (SoC) method is essential for an efficient operation of the VFB.

Since the first development of a VFB in the 1980s [4], many different methods for SoC monitoring were investigated. Widely used is the observation of the open circuit voltage (OCV). The OCV changes from about 0.6 V to 1.6 V during charging [5] and thus can be used as an easy and cheap method for SoC monitoring in commercial systems [6,7]. Nevertheless, the cell voltage is very sensitive to other influences such as the temperature; therefore, only approximate results can be obtained with this method. In addition, information about the state of the two half cells cannot be derived from the OCV, as it only observes the complete battery. For a more detailed investigation of both electrolytes, half cell potential or conductivity measurements can be used. Skyllas-Kazacos and Kazacos [8] developed a correlation between the SoC and the electrolyte conductivity. However, these parameters are very sensitive to other factors as well, as they change with temperature, total vanadium, and sulfur concentration shifts. Other methods are based on optical measurements; for example UV-visible light spectroscopy, which can be used for the SoC measurement in the negative electrolyte [8]. Buckley et al. [9] examined the absorption in the positive electrolyte in more detail followed by the development of an analytical model by Petchsingh et al. [10], also using UV-vis spectroscopy. Liu et al. instead used the transmission spectra to measure the SoC in the positive and negative electrolyte [11–13], while Rudolph et al. proposed monitoring the SoC by a new sensor principle using infrared absorption [14]. Despite problems with the measurement in the positive electrolyte, the optical methods are able to provide reliable values to observe the state of the battery. Nevertheless, all these principles need a complex calibration, due to the non-linear relationship between absorbed light and the individual vanadium concentration. Moreover, complex additional equipment is required. Other methods for SoC monitoring are based on further electrolyte properties, e.g., the change of viscosity proposed by Li et al. [15] whereas Ressel et al. [16] utilized the electrolyte density. Chou et al. [17] proposed the use of an ultrasonic velocity sensing method, which was previously employed for Li-ion batteries. Another completely new approach was the development of a four-pole cell device by Ngamsai et al. [18] to measure the ionic resistance of the electrolyte directly. Lawton et al. [19,20] proposed the use of electron paramagnetic resonance for the detection of V(IV) ions to investigate the vanadium crossover and vanadium uptake by the membrane. As this measurement technique requires complex and expensive technical equipment, it is not suitable for economical use in large-scale applications. Further recently published methods take advantage of mathematical modeling as described by Skyllas-Kazacos and coworkers [21–25]. These methods can help to control the overall cell performance, but they are not able to provide detailed information about the individual electrolyte, as required for an optimized monitoring system.

To summarize, there is still need for a new SoC measurement principle, which is able to monitor the two half cells individually and ideally determine the concentrations of each vanadium species. This is especially if the positive electrolyte remains difficult to analyze, for example through optical measurements, as mentioned above. For this purpose, amperometry is a promising candidate, as it is already a very common sensing principle in other fields. For instance, oxygen sensors for water analysis [26] or carbon dioxide sensors [27] are based on this concept. During these measurements, a constant potential is applied and the current answer is measured. The current is then linked to the active species concentration in the investigated solution. A mandatory prerequisite is a constant diffusion limitation of the measured current. Various methods can be employed to ensure this—the use of glassy carbon rotating disc electrodes (RDEs) is widespread, as the rotation guarantees the formation of a constant diffusion layer in front of the electrode [28] (pp. 193–197).

Therefore, the suitability of the amperometric measuring principle for the charge state measurement in the positive electrolyte is investigated in this work. The first step is to verify the basic applicability in the vanadium system. Applying a constant potential causes a reduction or oxidation current, depending on the potential value. When oxidative current flow is present, the V(IV) species are oxidized to V(V) species and vice versa. This results in a decrease of the respective species in front of the electrode, ideally to zero (Figure 1).
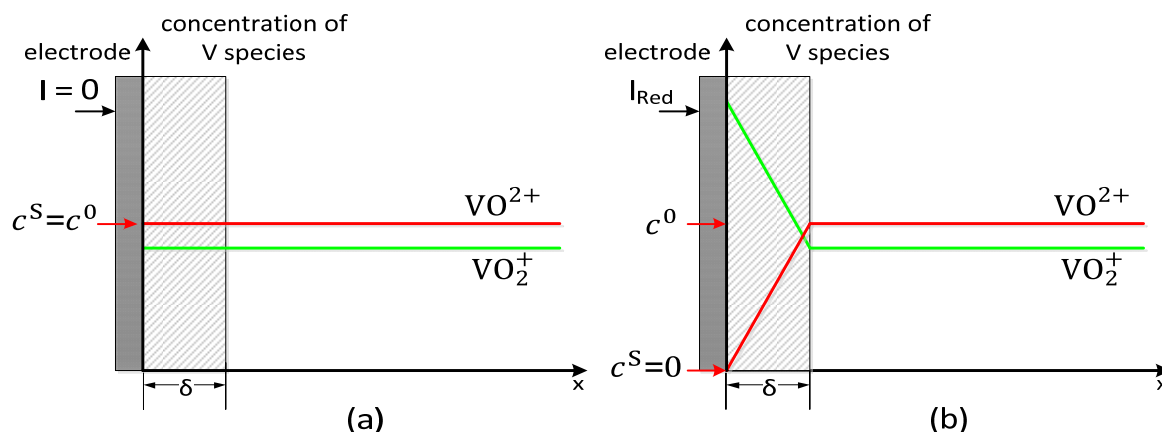
Figure 1. Concentration profile in the diffusion layer in front of the electrode in the positive electrolyte, without current (**a**) and with applied reduction current (**b**).

The resulting current density depends on the bulk concentration c^0, the surface concentration c^S and the diffusion layer thickness δ according to Fick's Law (see Equation (1), [28]). In addition, the equation also contains the charge number n, the Faraday constant F and the diffusion coefficient D. However, if the surface concentration decreases to zero and the diffusion layer thickness remains constant, the limiting current density j_{lim} depends only on the bulk concentration (see Equation (2)). Thus, the measured current can be used to determine the species concentration.

$$j = nFD\frac{c^0 - c^S}{\delta} \tag{1}$$

$$j_{\text{lim}} = nFD\frac{c^0}{\delta} \tag{2}$$

There are several ways to achieve a constant diffusion layer; the most common one is the use of a RDE. The constant rotation leads to the formation of a stable diffusion layer, depending on the rotation speed. Therefore, the RDE is a suitable method for the first investigation. For further application of this principle, especially regarding an on-line implementation, the RDE is not appropriate. An alternative method to achieve a constant diffusion layer is a fixed layer in front of the electrode, for example a porous ceramic layer. If the porous system is sufficiently thick, it ensures that there is no convective or migrative transport of ions to the electrode surface. This approach can therefore also be used as a possibility for the application of the amperometric method.

2. Results

2.1. RDE Results

For the proof of principle, cyclic voltammetry (CV) measurements were carried out with a glassy carbon RDE in the positive electrolyte. Therefore, the potential was varied between ± 1 V vs. OCV with 20 mV·s^{-1} scan rate. The tests started with positive vanadium electrolyte solution with a SoC of approximately 100%. The solution was then discharged stepwise by addition of the pristine electrolyte (equimolar solution of V(III)/V(IV)), with CV measurements in between. The exact values of vanadium concentrations and SoC were determined by redox titration in each step. The recorded reduction currents for different SoCs are shown in Figure 2. It can be easily seen that stable current plateaus are formed. This indicates that the resulting current is limited by diffusion, which means that there is a constant diffusion layer in front of the RDE. In addition, the current increases with rising SoC, respectively, V(V) concentration. For a detailed investigation of the relationship between SoC and current, the current values between -0.8 V and -0.85 V from the first half of the cycle are averaged and plotted against the SoC (see Figure 2b) showing a clear linear correlation. In Figure 2c the oxidation

current for different SoCs are shown. Stable current plateaus are also formed, even if a clear hysteresis is also visible. Due to the fact that used current values originate from the first half of the cycles, the hysteresis does not affect the results. This also ensures repeatability of the results. The oxidation current decreases with greater SoC values and therefore a reduced V(IV) concentration. Again, a linear relationship between the current values and the SoC can be seen here (see Figure 2d). In order to calculate the accuracy of the linear correlation obtained, the coefficient of determination r^2 is used as valuation factor. The coefficient of determination for the linear regression is 0.9966 for the reduction current and 0.9955 for the oxidation current.
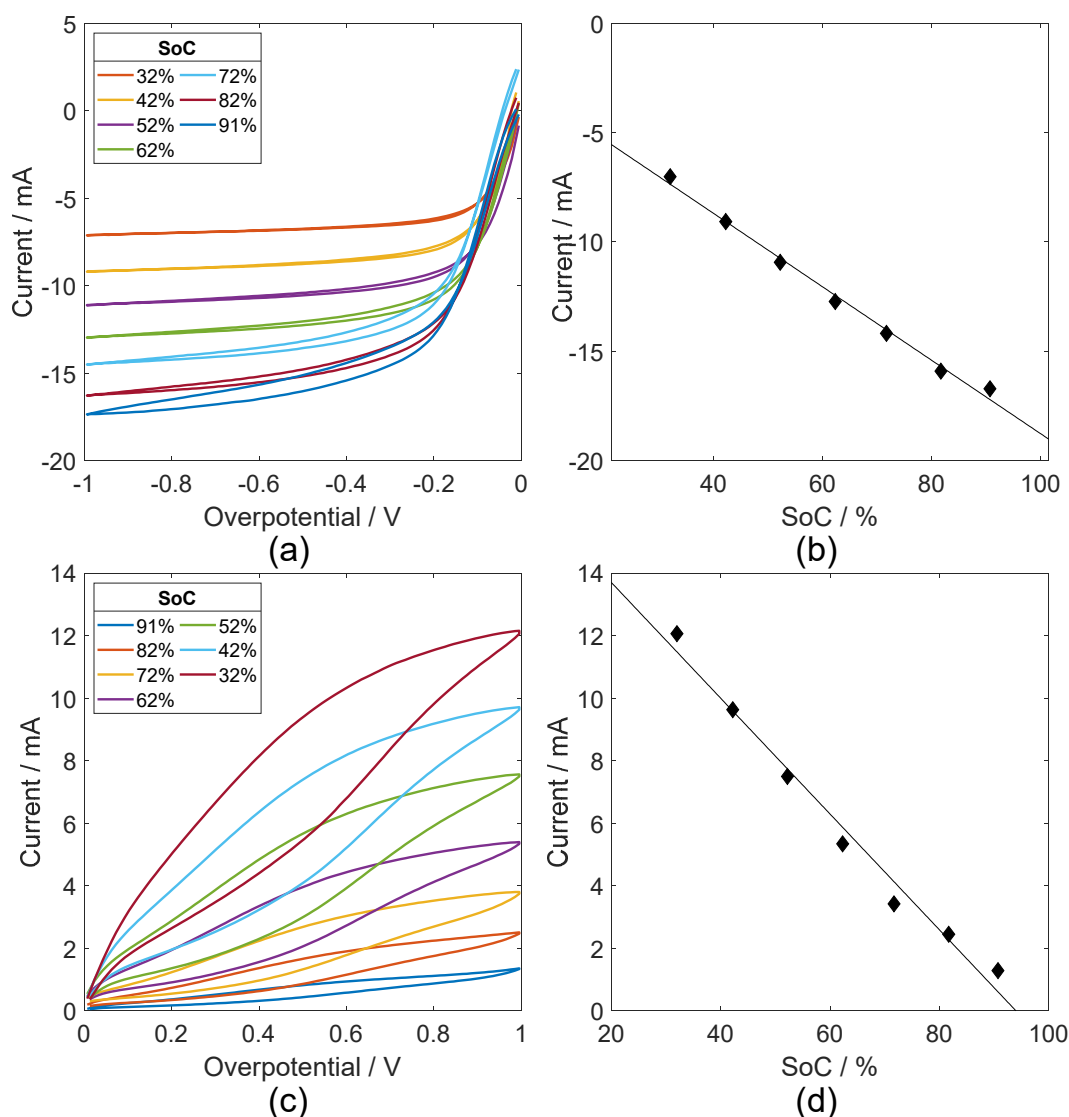

Figure 2. Results of cyclic voltammetry (CV) measurements with glassy carbon rotating disc electrodes (RDE) in positive electrolyte with different states of charge (SoCs), reduction current curves (**a**), reduction current values versus SoC (**b**), oxidation current curves (**c**), oxidation current values versus SoC (**d**) (scan rate 20 mV/s, platinum pseudo reference, diameter active area 5 mm).

2.2. Sensor Development

After ensuring that the principle works within the vanadium system, a suitable sensor was developed. The two most important requirements for such an amperometric sensor are a simple integration as an online measurement tool and a constant diffusion limitation. In addition, it should be easy to manufacture and cost-efficient. As active material for the sensor, a gas diffusion layer (GDL) was used, which was further activated by an electrothermal method previously developed in our

research group [29]. This treatment provides comparable results to the usual thermal activation and ensures that the reactions on the surface take place sufficiently fast, thus the kinetics are not a limiting factor. The material was then coated with adhesive and silicone, with a left out space of 1×1 cm^2 to create a specific active area. In the last step, the defined diffusion layer on top of the GDL was formed. For this purpose, porous ceramic layers were applied to the sensor by spray coating. Subsequently, the layer was cured by thermal treatment in an oven. The stepwise production of the sensor is shown in Figure 3. The porous ceramic layer works as a forced diffusion layer, which ensures that the resulting current is defined by the diffusion velocity of the ions through the ceramic layer.
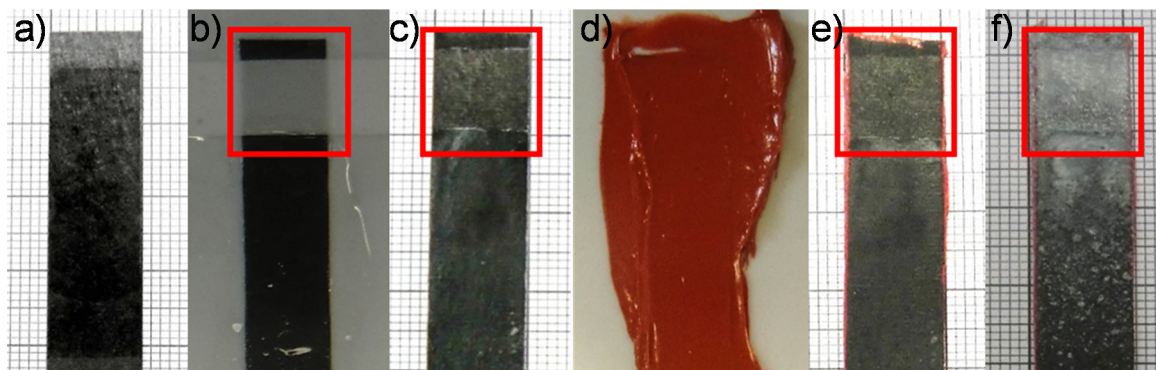

Figure 3. Manufacturing of the sensor (**a**) activated material, (**b**) coating with glue, (**c**) limited active area, (**d**) silicone coated back, (**e**) bare sensor, (**f**) active area with ceramic layer.

In order to find the most suitable solution for creating such a layer, various solutions were tested. For detailed investigation, bare sensors were coated with the three most promising solutions and tested in CV measurements. The experiments were carried out analogous to the RDE tests. The recorded CV curves are shown in Figure 4. It can be easily seen that the HS-40 solution (blue lines) leads to the most stable current plateaus; therefore, this solution is used for the further experiments.
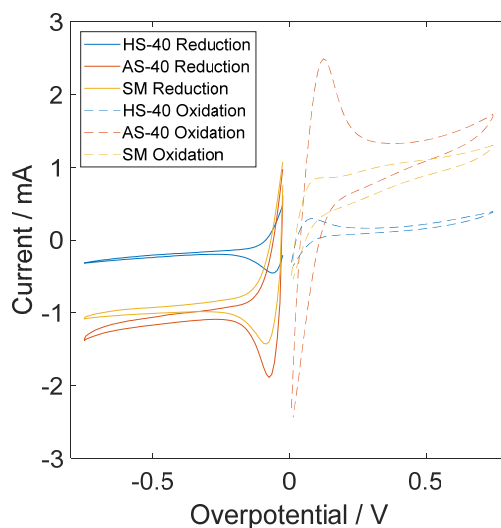

Figure 4. Results of CV measurements with sensor in positive electrolyte with different coatings.

2.3. Sensor Results

The first tests with the coated sensors were carried out in the same way as with the RDE. However, the potential range was reduced to ± 0.75 V vs. OCV, as this accelerated the measurement. The CV curves for different SoCs are shown in Figure 5a,c where stable current plateaus the values of which depend on the SoC can be seen. Once more, the current values were averaged between 0.7 V and 0.75 V.

Since only the values from the first half of the cycle were taken into account, the hysteresis effects do not influence the results and repeatability was ensured. For better evaluation, the results were plotted against the respective species concentration. Accordingly, the oxidation current was plotted versus the V(IV) concentration and the reduction current as a function of the V(V) concentration (see Figure 5b,d). It can be seen that accurate linear correlations for the relationship between the resulting current and the species concentration were obtained. The coefficient of determination for these regressions were 0.9993 (reduction current) and 0.9970 (oxidation current), thus the accuracy for the reduction current is slightly higher.
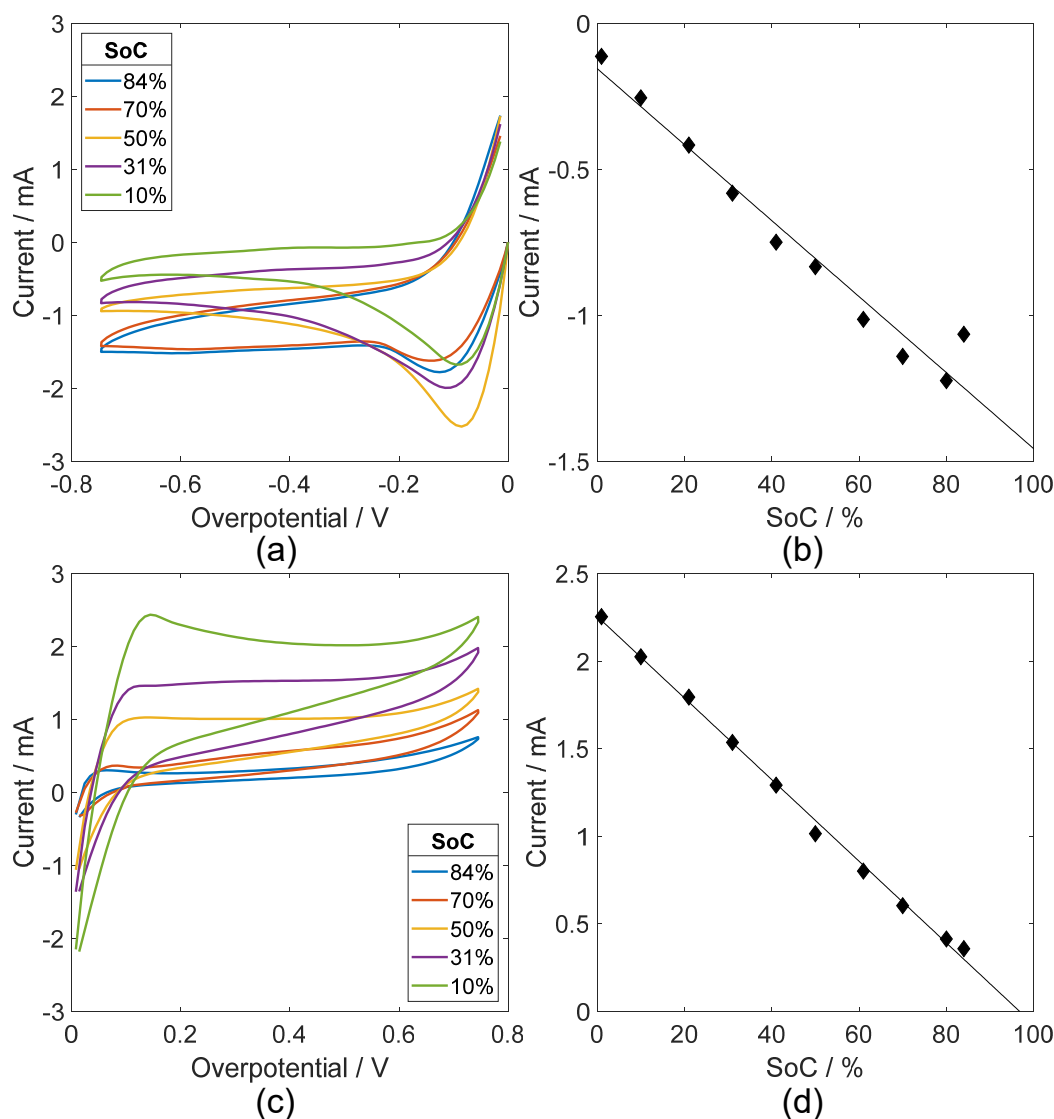

Figure 5. Results of CV measurements with sensor in positive electrolyte with different SoCs; reduction current curves; (**a**) current values versus SoC, (**b**) oxidation current curves, (**c**) current values versus SoC, (**d**) (scan rate 20 mV/s, platinum pseudo reference, active area 1 cm^2).

The CV measurements used for the proof of principle cannot be used for online SoC monitoring, as the tests take up to 20 min and have to be evaluated very elaborately. Thus, further tests were carried out using chronoamperometric (CA) measurements. A constant potential of ± 0.7 V vs. OCV was applied and the current answer was measured over time. The results for different SoCs are depicted in Figure 6a,c. After 100–120 s stable current response values were achieved. Thus, the CA method is significantly faster than the previously described CV measurements. It is also apparent that the current again increases or decreases with the SoC, depending on whether oxidative or reductive

current is considered. For further investigations, the current values (after 120 s) are again plotted against the individual vanadium species concentration (see Figure 6b,c). The results show a good linear correlation for the CA measurements as well. However, if one compares the results shown in Figure 6b,d, it becomes obvious that the accuracy obtained with the reduction current is significantly higher than for to the oxidation current.
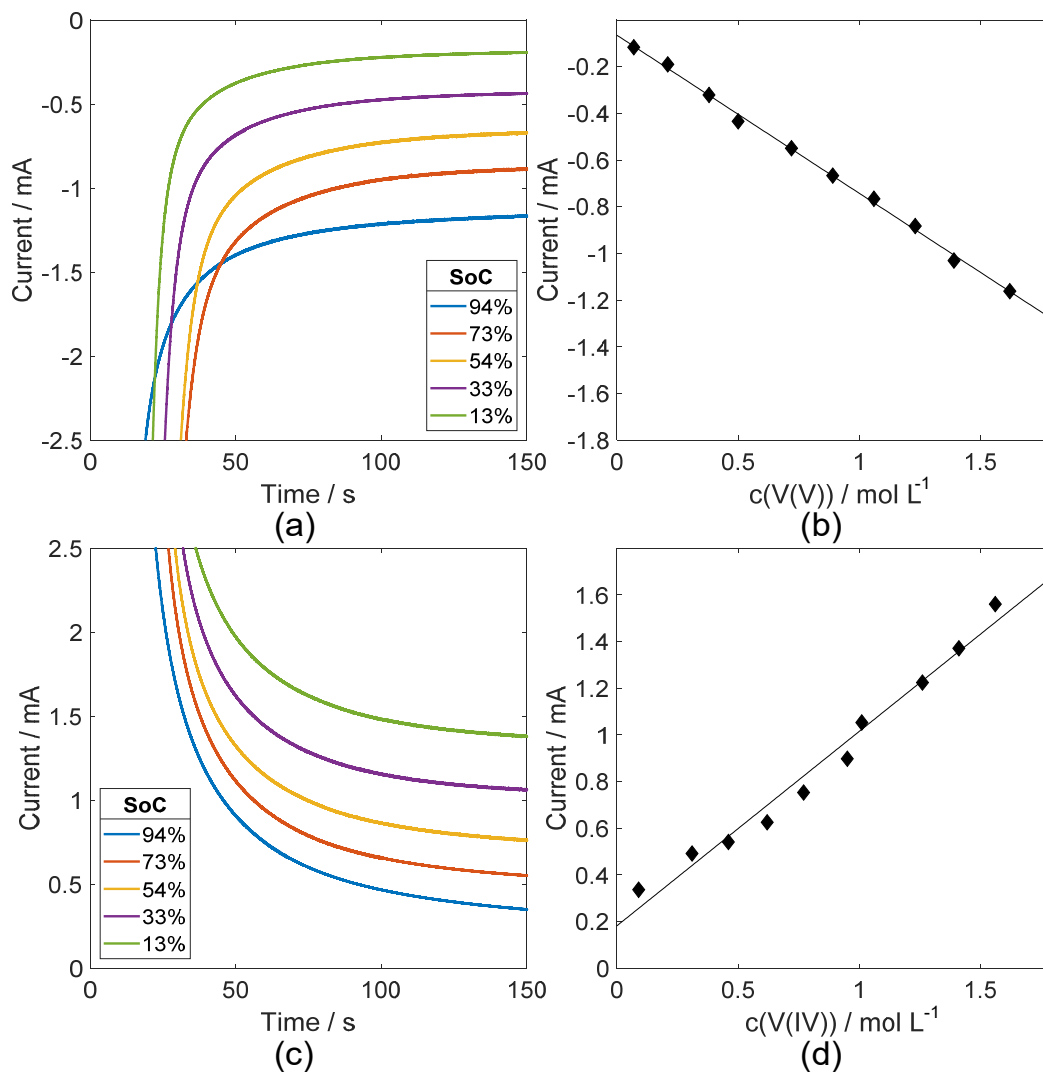

Figure 6. Results of chronoamperometric (CA) measurements with sensor in positive electrolyte with different SoCs; reduction current curves (**a**); current values versus SoC (**b**); oxidation current curves (**c**), current values versus SoC (**d**) (± 0.7 V vs. open circuit voltage (OCV), platinum pseudo reference, active area 1 cm^2).

3. Discussion

The measurements show that the amperometric principle is very well suited to SoC monitoring. A stable diffusion limitation can be achieved by coating of a carbon electrode with a ceramic layer, resulting in a linear correlation between active species concentration and current. It is possible to determine the V(V) concentration by applying the reduction current with very high accuracy ($r^2 = 0.9979$). Since it is possible to determine the V(IV) concentration with the oxidation current in the same manner, the total vanadium concentration can be also calculated. Although the V(IV) correlation has a slightly lower accuracy ($r^2 = 0.9761$), the proposed method can be used for SoC monitoring.

For this purpose, the V(V) concentration should be used as the main measurement value. Due to cross-over or side reactions, a change in the V(V) concentration cannot only be caused by a change in

the SoC. Therefore, an increasing reduction current answer is not directly implying an increasing SoC. To avoid such a misinterpretation, the oxidation current can be used to cross-check the results. If not only the SoC changes but also the total vanadium concentration, the shift in the oxidation current implies that the V(IV) concentration is changing as well. By offsetting the two current responses a more precise SoC estimation is possible.

The CA method allows for a very fast determination of the measured values, so that the SoC can be simultaneously obtained. The measuring time of about 120 s may be too long for some applications. At least for large-scale plants with long charge-discharge cycles, where the charge state does not change too quickly, this method is suitable. Moreover, this method does not necessarily require complex equipment, as the measurement can be carried out with the aid of simple constant voltage sources and current measurement and does not require a potentiostat. This also allows its use in large-scale commercial plants, since its use in large quantities is inexpensive.

Nevertheless, the current answer is still depending on other factors, as the diffusion current is also influenced by temperature or the proton and sulfate concentrations. These dependencies can be investigated in further work. Based on the results, a mathematical model can be developed with which the influence of these factors can be corrected. Another possibility would be the combination of the amperometric principle with a second method, e.g., the electrolyte density measurement. With the results from two independently operating methods, a redundant system can be built. Mathematical models can then be used to balance the influence of external factors and to avoid deviations.

4. Materials and Methods

All measurements are carried out with vanadium electrolyte from GfE Gesellschaft für Elektrometallurgie mbH, Nürnberg, Germany, with 1.6 mol·L^{-1} total vanadium and 4 mol·L^{-1} sulfuric acid, which consists of an equimolar mixture of V(IV) and V(III). A single cell setup is used to charge the electrolytes to 100% SoC, which corresponds to a V(II) solution in the negative and a V(V) solution in the positive electrolyte. For the first measurements, a glassy carbon RDE by Pine Research Instrumentation is used in a common three electrode set-up (see Figure 7a) for CV in vanadium electrolyte ($\pm$0.5 V vs. OCV; 20 mV/s). The measurements are carried out in a 100 mL round bottom flask, filled with vanadium electrolyte (55 mL). Platinum wire and mesh are used as counter and pseudo-reference electrode. All electrodes are connected to a Biologic SP-50 potentiostat to carry out the measurements.
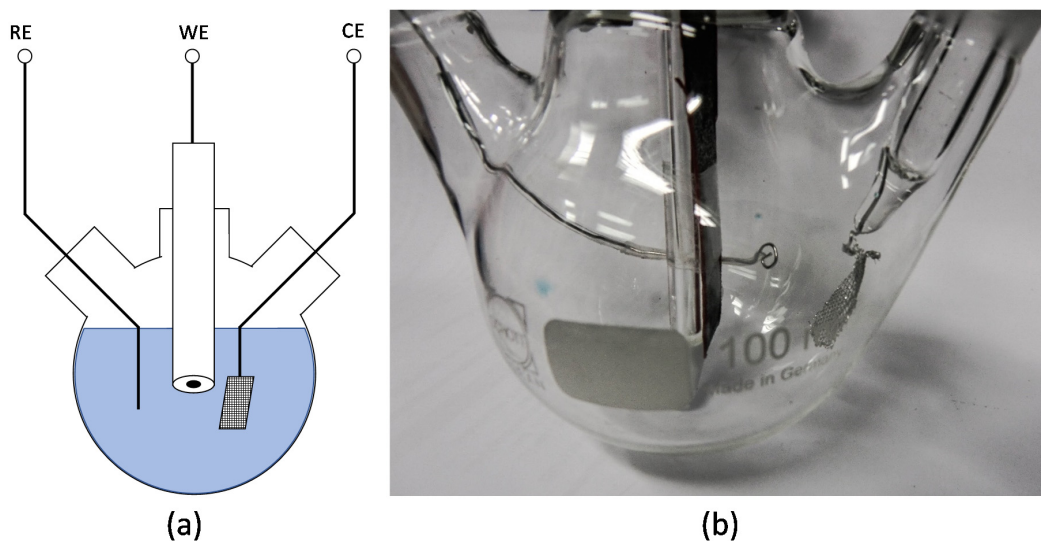

(a)　　　　　　　　　　　　　　　　　　　　　(b)

Figure 7. Experimental setup of rotating disc electrode (RDE) (**a**) and sensor (**b**) measurements, with RDE (diameter active area 5 mm) or sensor (active area 1 cm^2) as working electrode (WE), platinum mesh (approx. 2 cm^2) as counter electrode (CE) and platinum wire as reference electrode (RE), electrolyte volume during measurement 55 mL.

The used GDL for manufacturing of the sensor is a H2315 GDL by Freudenberg SE. The ceramic layers are applied with an airbrush gun from Revell. The three most promising solutions are HS-40, AS-40 and SM, which all are commercially available colloidal silica (SiO_2) suspensions by Ludox. Heat treatment of the complete sensor is carried out at 150 °C for 30 min in an air oven. The testing of the sensors is carried out analogously to the tests with the RDE, but with the sensor as working electrode (see Figure 7b).

CV measurements are also made at defined SoC values of the positive electrolyte, starting with 100%. The exact condition of the solutions is evaluated by redox titration again. In addition, chronoamperometry (CA) measurements are carried out with the sensor. Therefore, a potential of $\pm$ 0.7 V vs. OCV is applied and the resulting current is measured.

For each individual measuring point the electrolyte solution is investigated with a Metrohm Titrando 888, which performs a redox back titration with potassium permanganate solution (0.1 mol·L^{-1}) and an ammonium iron(II) sulfate (0.1 mol·L^{-1}) in sulfuric acid (1 mol·L^{-1}) [30]. This method was already used earlier in our research group; see Becker et al. [31] for more details. With this method, the exact condition of the electrolyte can be determined, i.e., total vanadium concentration, individual species concentration, and therefore, SoC.

5. Conclusions

In the present work, we propose a sensor based on the amperometric principle for the SoC monitoring in the positive electrolyte of a vanadium VFB. The sensor consists out of an electrothermally activated GDL and a ceramic layer on the active area. The ceramic layer works as a forced diffusion layer, which ensures that diffusion is the limiting factor. Thereby, the current answer for the application of a constant potential is directly linked to the species concentration in the vanadium electrolyte. More precise, the measured oxidative current is used to measure the V(IV) concentration while the reductive current represents the V(V) concentration. The correlation for the V(V) ions is in fact more accurate; therefore, it should be applied for SoC monitoring. Nevertheless, the oxidation current can be used for a counter-checking of the results, to make sure that a changing reduction current is not induced by a shift in the total vanadium concentration. The sensor can be operated directly inside the tanks, thus no sampling is needed. The principle is suitable as an online method to detect electrolyte imbalances and to compensate for these by appropriate capacity balancing strategies.

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