Monitoring the State-of-Charge in All-Iron Aqueous Redox Flow Batteries

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Monitoring the state-of-charge (SOC) in redox flow batteries is indispensable as a diagnosis tool to detect changes in the electrolyte concentration that can deteriorate the battery performance. Existing methods, which measure electrical variables of the cell or are dependent on recalibration during battery operation, become time consuming for practical uses. Here we present a simple and absolute method to monitor the SOC in iron aqueous redox flow batteries. The method is based on the determination of the Fe(II) concentration with photometry after forming the complex of Fe(II)-1,10-phenanthroline. It can be applied in both the negative and positive electrolytes, and it is independent of the pH, concentration, and temperature of the electrolytes. The SOC values are compared with the redox potential of the negative electrolyte during chronopotentiometry experiments using different cells in a ferro/ferricyanide (positive electrolyte) and Fe(III)/(II)-triethanolamine (negative electrolyte) system. The SOC values as a function of the redox potential measurements follow a Nernst equation, which demonstrates the validity of the method.

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Experimental

The chemicals used were of analytical grade quality: sodium hydroxide (NaOH, ≥ 99% p.a., Roth, Karlsruhe, Germany), ammonium acetate (NH₄CH₂CO₂, ≥ 97% p.a., Roth, Karlsruhe, Germany), acetic acid (CH₃COOH, 100% extra pure, 1.05 g/mL, Roth, Karlsruhe, Germany), 1,10-phenanthroline (1,10-phenanthrolinium chloride monohydrate, C₁₂H₁₄N₂·HCl·H₂O, ≥ 99.5% p.a., Merck, Darmstadt, Germany), hydroxylamine hydrochloride (hydroxyaminommonium chloride, CH₃NO, ≥ 99.5% p.a., Roth, Karlsruhe, Germany), potassium ferrocyanide (K₄[Fe(CN)₆]), 3H₂O, ≥ 99% p.a., Sigma-Aldrich, Steinheim, Germany), and sulfuric acid (H₂SO₄, with 96 wt% content in water, 1.84 g/mL, Deuring, Hörbranz, Austria). Ferric chloride (FeCl₃, with 39 wt% content in water, 1.42 g/mL, Deuring, Hörbranz, Austria), and triethanolamine (TEA, with 85 wt% content in water, 1.42 g/mL, Deuring, Hörbranz, Austria) were of technical grade quality.

The composition of the negative electrolyte, Fe(III)-TEA, was 0.2 M FeCl₃, 0.9 M TEA and 1.3 M NaOH. The solvent was deionized water. For the preparation of the negative electrolyte, FeCl₃ was first placed in a beaker with a magnetic stirrer bar, and then NaOH and TEA were added fast and at the same time to the FeCl₃. The solution was left under stirring for half an hour. The concentration of TEA was chosen to be four times higher than the concentration of iron to guarantee sufficient stability of the cathodically formed Fe(II)-TEA complex in alkaline media, and therefore to avoid precipitation and deposition of iron(II) hydroxide on the electrodes. The container of the negative electrolyte had a volume of 12.5 mL, pH 13.3 and a conductivity of 204 mS cm⁻¹.

The composition of the positive electrolyte, Fe(II)-CN, was 0.4 M potassium ferrocyanide in 0.4 M NaOH. The solvent was deionized water. The container of the positive electrolyte had a volume of 30 mL, pH 13.7 and a conductivity of 192 mS cm⁻¹. The cell was designed to be asymmetric (the concentration and volume of the positive electrolyte were larger than the negative electrolyte) for a rapid turnover only dependent on the total amount of the negative electrolyte, and to ensure the operation of the cell regardless of the presence of some accumulation of electrolyte at the negative electrode. The electrolyte densities were measured by measuring half-cell potentials and electrolyte densities, which need to be measured under steady-state conditions,2 which include the operation of the cell regardless of the presence of some accumulation of electrolyte at the negative electrode. The electrolyte densities were measured by measuring half-cell potentials and electrolyte densities, which need to be measured under steady-state conditions,2 which include the operation of the cell.
oxygen. Solutions were aerated for 10 min with argon before the experiments.

Figure 1a shows a schematic drawing of the experimental setup. The cell was composed of four polycarbonate frames of 5 mm thickness forming two electrode compartments separated by a Nafion cation-exchange membrane (thickness of 450 μm, provided by De Nora Rodenbach, Germany) and held with silicone sealant. The cell contained embroidered stainless steel electrodes for each compartment, which also acted as the current feeders (no need of current collectors).

The SOC determination was performed using three different cells prepared with embroidered electrodes showing different surface areas (of about 2.8 cm² and 4.2 cm²) and porosities (of about 10% and 65%). Photomicrographs of the embroidered electrodes are provided in Figure S3 in the Supplementary Information. A picture of the cell constructed with the embroidered electrodes is shown in Figure 1b.

Cyclic voltammograms (CVs) using as working electrodes, a hanging mercury drop electrode (HMDE), a platinum (Pt) disc electrode, and a stainless steel yarn (SST), were obtained with a Princeton Applied Research Model 264A polarographic analyzer. Ag/AgCl (3 M KCl) was used as reference electrode and a platinum wire as counter electrode. The SST yarn used for the CVs was composed by filaments of 8 μm in diameter held together with a polyester yarn (1/3 of the total volume) forming a tight yarn with a total diameter of 360 μm. The length was about 6.8 mm, which corresponded to a solid cylindrical surface area of 7.69 · 10⁻² cm².

The photometry experiments for the SOC determination were performed using a reference Ag/AgCl (saturated KCl) electrode placed in the Fe-TEA container to monitor the redox potential.

The photometric determination of Fe(II) was performed by measuring the 1,10-phenanthroline absorbance at 520 nm. Three solutions (A, B and C) were required for the photometric measurements. Solution A, also called pre-diluted solution, was prepared by mixing rapidly 5 mL of 20 wt% sulfuric acid (0.012 mol of H₂SO₄), and 2 mL of the negative electrolyte with the unknown concentration of Fe(II) (0.04 mol of total iron), with deionized water to a total volume of 100 mL. Solution B was prepared by mixing 1 mL of solution A, 10 mL of the buffer, and 2 mL of 1,10-phenanthroline solution (0.04 mmol), with deionized water to a total volume of 100 mL. The buffer was prepared by mixing 50 g of ammonium acetate (0.669 mol), and 50 mL acetic acid (0.874 mol), with deionized water to a total volume of 250 mL. The pH of the buffer was 5. The 1,10-phenanthroline solution was prepared by dissolving 0.5 g of 1,10-phenanthroline chloride (0.002 mol) in deionized water to a total volume of 50 mL. Solution C was prepared by mixing 1 mL of solution A, 10 mL of the buffer, 2 mL of 1,10-phenanthroline solution (0.04 mmol), and 2 mL of hydroxylamine solution (1.4 mmol), with deionized water to a total volume of 100 mL. The hydroxylamine solution was prepared by dissolving 5 g hydroxylammonium chloride (0.035 mol) in deionized water to a total volume of 50 mL. A blank solution consisted of 5 mL of 20 wt% sulfuric acid (0.012 mol of H₂SO₄), 10 mL of the buffer, and 2 mL of the 1,10-phenanthroline solution (0.04 mmol), was also prepared.
The absorbance before photometric measurements, a waiting period of 10–15 min was required to ensure full oxidation of the compounds. The absorbance was measured at 520 nm in a 1 cm³ cuvette using a photometer Merck SQ300.

### Results and Discussion

The flow cell employs the Fe⁴⁺/Fe²⁺ redox couple for the negative and positive electrolytes. The redox reactions were investigated by cyclic voltammetry (Figure 2). The positive solution is denoted for convenience as Fe-CN or [Fe(CN)₆]⁴⁻ and the negative solution as Fe-TEA or Fe(III)/Fe(II)-TEA. The electrode reactions may be described as shown in Equation 1 and Equation 2:

\[
\text{Fe(III)} - \text{TEA} + e^- \rightleftharpoons \text{Fe(II)} - \text{TEA} \quad E^0 = \left( -1061 \pm 4 \right) \text{mV at pH 13.3} \tag{1}
\]

\[
[\text{Fe(CN)}₆]^{3-} \rightleftharpoons [\text{Fe(CN)}₆]^{4-} + e^- \quad E^0' = (289 \pm 5) \text{ mV at pH 13.7} \tag{2}
\]

where \(E^0\) is the formal potential obtained from Figure 1a using HMDE and Pt electrodes versus Ag/AgCl (3 M KCl) reference electrode.

Table 1 shows the electrochemical values obtained from Figure 2a and Figure 2b, respectively. Deviations from the reversible behavior using HMDE and Pt working electrodes are associated with the high concentrations of the 0.2 M Fe(III)-TEA and 0.4 M [Fe(CN)₆]⁴⁻ used in the system, since in previous investigations, dilute solutions with concentrations of about 50 mM or lower, showed reversible behavior. The formal reduction potential obtained with stainless steel electrodes, \(E^0' = (1063 \pm 12) \text{ mV}\), was very close to the one obtained with the HMDE, \(E^0' = (1061 \pm 4) \text{ mV}\).

Figure S1 and Figure S2 in Supplementary Material show schematic drawings with the possible chemical structures and reactions involved. The SST working electrode started to corrode at positive potentials when current densities are greater than 50 mA cm⁻². However, current densities used in our experiments (between 2–5 mA cm⁻²) for SOC determination were lower, and therefore corrosion could be neglected. The focus of using stainless steel embossed electrodes was to ensure different cell characteristics (electrode surface areas and porosities), and therefore different battery performances, to demonstrate that the method described in this work for the determination of SOC is independent of the battery performance.

The SOC was obtained from chemical analysis by using the organic compound 1,10-phenanthroline as complexing agent for the photometric determination of Fe(II) in solution B, and measuring its absorbance at 520 nm. Hydroxylamine was employed for the reduction of Fe(III) to obtain the absorbance corresponding to the total iron content after forming the complex Fe(II)-1,10-phenanthroline (photometric determination of Fe(II) in Solution C). The SOC values were calculated using the Beer-Lambert equation, which permits to relate Fe(II) and total iron concentrations with the measured absorbance.

During the SOC determination by photometry, the redox potential was monitored in the Fe-TEA electrolyte container during different chronopotentiometry experiments at room temperature using three different cells. The cells, because of the difference in electrode morphology, and therefore because of their differences in the cell resistivity, presented different cell potentials during the chronopotentiometry experiments (Figure 3). The experiments were performed at room temperature, at an applied current of 20 mA (current densities between 4–7 mA cm⁻² depending on the electrode surface area), at a volumetric flow rate of 30 mL min⁻¹, and at an average linear flow rate at the electrode of about 0.5 cm s⁻¹.

Figure 4 shows the dependence of the SOC obtained from the photometric measurements on the redox potential monitored during the chronopotentiometry experiments. The values followed a Nernst equation (\(R^2 = 0.97\)), \(E = E^0' + \Delta E^0 + (RT/nF) \ln(C_{\text{Fe(II)}}/C_{\text{Fe(III)}})\), with a

### Table 1. Data extracted from CV using standard working electrodes HMDE and Pt (Fig. 2a), and SST yarn (Fig. 2b). The cathodic/anodic peak current densities \(i_{cp}/i_{ap}\), ratio of reverse-to-forward peak current densities \(i_{rp}/i_{fp}\) and potentials \(E_{cp}, E_{ap}, E_{1/2}\) are listed.

| Scan rate (mV s⁻¹) | \(i_{cp}\) (mA cm⁻²) | \(i_{ap}\) (mA cm⁻²) | \(i_{rp}/i_{fp}\) | \(E_{cp}\) (mV) | \(E_{ap}\) (mV) | \(E_{1/2} = (E_{ap} + E_{cp})/2\) (mV) |
|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Fe-TEA (HMDE)     |                   |                   |                   |                   |                   |                   |
| 100               | 20.6              | −13.9             | 0.66              | −1366            | −767             | −1067             |
| 50                | 15.9              | −12.5             | 0.81              | −1308            | −813             | −1061             |
| 20                | 11.1              | −10.9             | 0.98              | −1242            | −880             | −1061             |
| 10                | 8.67              | −8.91             | 1.03              | −1207            | −911             | −1059             |
| 5                 | 7.23              | −7.67             | 1.06              | −1181            | −930             | −1056             |
| Fe-CN (Pt)        |                   |                   |                   |                   |                   |                   |
| 100               | 8.51              | −9.64             | 0.88              | 136              | 449              | 293               |
| 50                | 7.61              | −7.89             | 0.97              | 159              | 422              | 291               |
| 20                | 4.62              | −4.61             | 1.00              | 197              | 384              | 291               |
| 10                | 3.62              | −3.33             | 1.09              | 206              | 365              | 286               |
| 5                 | 3.09              | −2.75             | 1.12              | 208              | 363              | 286               |
| Fe-TEA (SST)      |                   |                   |                   |                   |                   |                   |
| 100               | 21.8              | −1.46             | 0.07              | −1272            | −865             | −1069             |
| 50                | 14.4              | −4.25             | 0.30              | −1226            | −895             | −1061             |
| 20                | 9.05              | −2.10             | 0.23              | −1227            | −892             | −1060             |
| 10                | 6.49              | −2.22             | 0.34              | −1206            | −913             | −1060             |

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formal potential of $E' = (-1000 \pm 6)$ mV. From the Nernst equation, a relationship between the SOC and redox potential can be extracted as follows considering no variations in temperature during the experiments (Equation 3):

$$SOC = \left[1 + \exp\left(\frac{nF(E - E'V)}{RT}\right)\right]^{-1} \cdot 100\% \quad [3]$$

where $C_{total\ iron} = 0.2$ M is the concentration of the total iron content in Fe-TEA container, $T = 300$ K, $E' = -1.0$ V is the formal reduction potential obtained from the fit, $n = 1$ is the number of electrons involved, $F$ and $R$ are the Faraday and gas constants.

The inset pictures at two different SOC reveal the color change to a darker orange when the amount of Fe(II) was increased. Although the data points were obtained from experiments with different cell performances, all SOC values follow the same Nernst equation, which demonstrates the validity of the method. The formal potential obtained from the fit, $E' = (-1000 \pm 6)$ mV, is 60 mV lower than the one obtained from the CVs in Figure 1b, which might be associated with the different reference electrodes (Ag/AgCl sat. KCl) and working electrodes (Pt disc electrode) used. A weak point in the calibration method may consist of a reading delay between the SOC inside the cell and the container, especially when the cell is comparable with the container volume or when the electrolyte flow rate is too low, which is not the case in large-scale applications.

Figure 4 also shows the SOC value obtained from chronopotentiometry experiments when the reduction went nearly to completion in cell 1. The maximum redox potential observed at the negative electrolyte was $-1066$ mV, which corresponded to an experimental time for the chronopotentiometry experiments of $t_{exp} = 3.16$ h. Longer charge times did not provide higher values, in contrast, side reactions started to occur, such as hydrogen/oxygen evolution, promoting a decrease of the current efficiency. The theoretical charge time for a complete reduction of the Fe(III)-TEA, calculated from Faraday’s law for 100% SOC was $t_{total} = 3.4$ h. The SOC, calculated as SOC = $t_{exp}/t_{total}$, was 93%. The SOC value followed the Nernst equation obtained from the photometry measurements, also confirming the validity of the photometric measurements for the SOC determination.

The new approach using photometry measurements after the formation of the 1,10-phenanthroline-iron complex provides the turnover of the cell obtained from chemical analysis instead of an indirect reading from electrical values of the cell, and it does not require the cell to be balanced as in the case of the OCV. Spectrophotometric principles are also commonly used to monitor the SOC in vanadium systems due to the different colors of the charged and discharged electrolytes. However, they require a previous calibration of the absorbance measurements with the electrolyte concentrations, and depending on the concentration and adsorption the calibration might not be either as feasible or as straightforward as expected. The method described here provides on one hand, the accuracy of the photometric measurements for the SOC determination, where their values are independent of drifts in the potential unlike OCV or half-cell measurements. On the other hand, the method is independent of the electrolyte concentration, pH or temperature, and can provide selectivity to distinguish crossover of species. The formation of the 1,10-phenanthroline complex with Fe(II) ion in the presence of cyanide was not favorable under our experimental conditions. Thus, the method using 1,10-phenanthroline cannot be applied for the SOC determination in the positive electrolyte Fe-CN in its present formulation. However, it could be useful for detecting crossover of Fe-TEA to the positive side through the membrane. Further investigations will be focused on the reformulation of the method, for instance to form Prussian Blue, for the SOC determination on the Fe-CN electrolyte. The photometric determination using 1,10-phenanthroline can also be extended to other chemistries, such as vanadium and chromium systems.

Conclusions

A simple and absolute method based on the photometric absorption of the reagent 1,10-phenanthroline for the determination of the SOC in iron aqueous redox flow cells is presented. The method was applied to the Fe$^{2+}$/Fe$^{3+}$ redox couple using as a negative electrolyte the Fe-TEA. The method could not be applied to the positive electrolyte the ferro/ferricyanide system in its present form, but it could be used for the selective detection of Fe-TEA crossover to the positive side. The SOC values were correlated with the redox potential measured in the negative electrolyte during chronopotentiometry experiments using three different cells. The SOC values versus the redox potential followed a Nernst equation with a formal potential very close to the previously obtained from cyclic voltammograms. This demonstrates the validity of the method.

The advantages of the method are the following:

- It is pH independent, since the solutions used for the SOC determination are buffered to a pH 5.
- Although the experiments were performed at room temperature, we expect no influence of the electrolyte temperature in the SOC determination. The pre-diluted solution, which is required for the determination of the Fe(II) and total iron concentration, was prepared using 2 mL of electrolyte diluted to 100 mL of solution at room temperature.
- The method can be extended to any system using the Fe(II)/Fe(III) redox couples, where 1,10-phenanthroline has a stronger Fe(II) complexing ability as compared to the original ligand. The iron must be soluble or ligand-bound.
- The method permits to detect the active species crossover. For each SOC value, apart from the Fe(II) concentration, the total iron Fe(II)+Fe(III) concentration is determined, and have to agree with the initial total iron concentration of the electrolyte. Also, it could be useful for detecting crossover of Fe-TEA to the positive side through the membrane.
- Matrix effects play a role when concentrations of copper, chromium or zinc are ten times larger than the iron concentration. Although these concentrations are unusual, matrix effects can be also avoided using internal standards.

The method presents the disadvantage that is not continuous, and the reagents have a lifetime of few weeks.
Acknowledgments

Authors thank Texible GmbH and the smart embroideries Austria for providing the embroidered current collectors. Authors also acknowledge support from the Standortagentur Tirol and State of Vorarlberg through the research project “Competence Sports Textiles”, and the K-Project TCCV Nr. 860474 funded by Federal Ministry for Transport, Innovation and Technology (BMVIT), Austrian Federal Ministry of Science, Research and Economy (BMWFW), Land Vorarlberg, Land Tirol, and Land Wien within the framework of COMET Competence Centers for Excellence Technologies. The COMET program is managed by the Austrian Research Promotion Agency (FFG).

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