Cycle behaviour of hydrogen bromine redox flow battery cells with bromine complexing agents

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HIGHLIGHTS

- [C2Py]Br as bromine complexing agent in safe posolytes for \( \text{H}_2/\text{Br}_2 \)-RFB.
- Two-phase electrolyte: bromine-poor aqueous phase and bromine-rich fused salt.
- Bromine half cell performance limitation due to formation of [C2Py]-fused salt.
- Membrane performance limitation due to interaction with [C2Py]\textsuperscript{+} cations.
- \( \text{Br}_2 \) crossover intensifies both effects due to release of BCA from fused salt.

ABSTRACT

Bromine complexing agents (BCA) are used to improve the safety of aqueous bromine electrolytes versus bromine outgassing in bromine electrolytes. In this work, cycling performance of hydrogen-bromine redox flow battery cells with 1-ethylpyridin-1-ium bromide ([C2Py]Br) as BCA in a bromine electrolyte with a theoretical capacity of 179.6 A h L\textsuperscript{-1} is investigated for the first time. The BCA leads to increased ohmic overvoltages. One cause of the ohmic drop can be attributed to [C2Py]\textsuperscript{+} cation interaction with the perfluorosulfonic acid (PFSA) membrane, which results in a drop of its conductivity. The BCA also interacts with bromine in the cell, by forming a non-aqueous fused salt second phase which exhibits a ten times lower conductivity compared to the aqueous electrolyte. A steep rise in cell voltage at the beginning of the charge curve followed by a regeneration of the cell voltage is attributed to this effect. Electrolyte crossover leads to an accumulation of [C2Py]\textsuperscript{+} in the electrolyte solution and intensifies both adverse processes. Under this condition only 30% of the theoretical electrolyte capacity of 179.6 A h L\textsuperscript{-1} is available under long term cycle conditions. However, electrolyte capacity is high enough to compete with other flow battery technologies.

1. Introduction

One opportunity for stationary energy storage are hydrogen-bromine redox flow batteries (\( \text{H}_2/\text{Br}_2 \)-RFB) \cite{1-5}, which are currently on the cusp of commercialization \cite{6,7}. \( \text{H}_2/\text{Br}_2 \)-RFBs use a hydrogen gas diffusion electrode like in polymer electrolyte membrane fuel cells and a
bromine/bromide half cell, which is operated with liquid electrolytes. Electrolytes are composed of hydrobromic acid (HBr), bromine (Br₂) and water and are pumped through the positive H₂/Br₂-RFB half cell. The principle of a H₂/Br₂-RFB is shown in Fig. 1/a. During charge, bromide (Br⁻) is converted to Br₂ by oxidation in the positive half cell. In the negative half cell protons (H⁺) are reduced to hydrogen (H₂) [3,4]. Discharging of the battery takes place in the same conversion unit, while the reactions proceed in opposite direction [3,4] according to equation Eq. (1) [4,11]. The open cell voltage at standard conditions is 1.09 V [8–10].

\[
\text{H}_2(g) + \text{Br}_2(aq) \xrightarrow{\text{Discharge operation}} 2 \text{HBr}(aq) \xrightarrow{\text{Charge operation}} \text{Discharge operation}
\]  

(1)

High possible molar substance concentrations in the electrolytes (e.g. 7.7 M HBr) lead to large useable capacities of 179.6 A h L⁻¹ [12]. Also high power densities can be reached [3,13]. Both are raised due to fast reaction kinetics in both half cells and high concentrations of HBr and Br₂ [3,13]. Instead, other redox flow battery (RFB) types like vanadium-RFB are limited in their volumetric electrolyte energy density of around 26.8 Wh L⁻¹/21.4 A h L⁻¹ [6] and in zinc bromine RFB (Zn/Br₂-RFB) the zinc deposition on the electrode surface limits the storage capacity [14,15].

The high solubility of unpolar Br₂ in HBr solutions [16,17] is reached due to the formation of so-called polybromides Br₂n⁻ like tri-, pentabromides according ref. [5,8,12,18–21]. Those are bound by addition bonds to the bromine ion [22]. Nevertheless, bromine remains highly volatile due to its high vapour pressure [23–25] and is toxic by skin contact and inhalation [15,26]. In order to achieve safe and high energy density battery electrolytes, bromine complexing agents (BCA) are applied to reduce vapour pressure of bromine in aqueous solutions [24]. There, mainly BCAs from the group of quaternary ammonium salts are used as complexing agents [27–32]. Common substances, which are mainly applied in Zn/Br₂-RFB since the 1970s are 1-ethyl-1-methylpyrroldin-1-ium bromide [MEP]Br and 1-ethyl-1-methylmorpholin-1-ium bromide [MEM]Br [14,26–28,32–42]. Next to [MEP]Br and [MEM]Br there is a wide range of possible BCAs based on quaternary ammonia moiety, which are made from N-heterocycles [14,26,28,31,32,37,38,41,42]. 1-ethylpyridin-1-ium bromide [C2Py]Br (Fig. 1/b) is a cost effective BCA and is suggested by other authors due to moderate sequestration and lower polarization effects in the cell compared to other BCAs [14,41], but only investigated for Zn/Br₂-RFB application with a focus on zinc deposition. The functionality of these BCAs is based on the obtained solubility of the BCA-bromide salt while precipitation of BCA-polybromide salts occurs according to Eq. (2) [22,27,31], resulting in the formation of an additional phase as shown in Fig. 1/a for the example of [C2Py]Br. This phase does not form a solid, but a second

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Fig. 1. (a) Schematic drawing of assembly and operation of a H₂/Br₂-RFB single cell ((1) hydrogen gas diffusion half cell, (2) positive bromine half cell, (3) PFSA membrane, (4) proton exchange through membrane) with inserted photograph showing the phase compositions of a bromine electrolyte with BCA containing (5) Br₂ in gas phase, (6) aqueous electrolyte phase and (7) fused salt in a glass tank and (b) structural formula of the applied BCA 1-ethylpyridin-1-ium bromide [C2Py]Br.
liquid phase [14,41] at room temperature, very similar to a deep eutectic phase, and is called fused salt. It deposits below the aqueous solution due to its high density (Fig. 1/a) [31]. During charge and discharge experiments, polybromides, [C2Py]+ cations and bromide are distributed across two different phases based on Eq. (2):

\[ \text{[C2Py]}^+ (aq) + \text{Br}_{2n+1}^-(aq) = \text{[C2Py]}\text{Br}_{2n+1} (s) \downarrow \]

The application of BCAs in acidic solution for H2/Br2-RFB has not been investigated in detail. No comprehensive study on cycling tests with [C2Py]Br or further BCAs in electrolytes for H2/Br2-RFB has been presented in the literature so far, with the aim of achieving a durable battery cycleability and considering an electrolyte with a large theoretical capacity of 179.6 A h L\(^{-1}\) and a large theoretical energy density of 195.8 Wh L\(^{-1}\). A dependence of the processes in cell based on Eq. (2) and on the state of charge (SoC) considering the associated electrolyte compositions has not been investigated in a cell test so far.

In this study we investigate the influence of the bromine complexing agent [C2Py]Br on the cell performance of a H2/Br2-RFB single cell. High energy density electrolyte with a theoretical capacity of 179.6 A h L\(^{-1}\) is chosen. Cycling experiments along the capacity range are determined for different electrolytes. Visible phenomena caused of [C2Py]Br and their influence on the cell performance are determined in analytical methods online and in ex situ investigations on electrolyte composition. This study focuses especially on the comparison between [C2Py]Br concentrations and cell performance, and effects on further parameters like electrolyte conductivity, bromine concentrations and cell resistances. The work provides a detailed investigation on challenges in the application of quaternary ammonium compounds as BCAs in the bromine half cell of a H2/Br2-RFB. In Section 2 experimental methods are described for this purpose. Results are presented and discussed in Section 3.

2. Experimental and methods

A detailed version of the chapter “Experimental and methods” is available in the Electronic Supplementary Information (ESI). Here, individual methods are described in detail in order to allow for experiments to be reproduced. Furthermore, substances and materials used, their suppliers, purity, measurement setup and NMR characterization of the synthesized [C2Py]Br can also be found in the ESI.

2.1. Electrolyte preparation

Bromine electrolytes base on HBr 48 wt% and Br2 in aqueous solution. The targeted capacity is specified by the composition at different state of charge (SoC): SoC 0% with 7.7 M HBr and SoC 100% with 1 M HBr and 3.35 M Br2. The definition of the SoC range is based on an work in earlier literature [12] concerning BCA-free HBr/Br2/H2O electrolytes. The concentration of the [C2Py]Br is 1.11 M for all BCA-containing electrolyte samples. The choice of BCA concentration depends on the molar ratio of Br2 to BCA at certain SoCs. A ratio of 3:1 between Br2 and BCA is received at SoC 100%, representing theoretically one molecule heptabromide Br7 for each BCA molecule in solution. At SoC 33% respectively a ratio of 1:1 between Br2 and BCA is received, expecting all Br2 to be available as tribromide Br3, [C2Py]Br3 is prepared from pyridine and bromoethane by alkylation [43,44] according to Dzyuba et al. [45] and dried in a vacuum chamber. 1H NMR and 31P NMR (attached in ESI) are recorded for [C2Py]Br and confirmed by existing literature [44]. [C2Py]Br is solved in water and HBr 49 wt% and after Br2 is added. Equilibrium of the components across the two phases is reached by mixing electrolyte samples each day once or one week. For ex situ investigation of electrolyte properties 30 mL samples of electrolytes at SoC 0, 33, 60, 67, 70, 80, 90 and 100% are mixed. For all cycling tests 90 mL of electrolyte at SoC 100% are prepared. Choice of SoC for the investigated samples is based on the investigated SoC range in cell tests (Section 2.6). All measurements on the electrolytes are carried out at a temperature of \(\theta = 23\, {^\circ}\text{C} \pm 1\, {^\circ}\text{C}\).

2.2. Electrolyte conductivities

Electrolyte conductivities of aqueous electrolyte solutions and fused salts for SoC 0, 33, 60, 67, 70, 80, 90 and 100% are investigated by linear chronamperometry at a rotating disk electrode. At a rotation speed \(\omega = 1000\) rpm on vitreous carbon electrode, linear sweep excitations between 0.8 V and \(-0.5\) V vs. Ag/AgCl/KCl(sat.) reference electrode (RE) and a scan rate of \(-40\) mV s\(^{-1}\) are performed. Constant reduction reaction currents result for potentials \(-0.1\) V vs. RE, which are independent of the applied potential. According to Levich [46–49], these reduction currents are directly proportional to the concentration \(c(Br2)\) of the bulk solution. Concentrations \(c(Br2)(aq) (\text{SoC})\) are calculated from the limiting currents \(I_{lim}(\text{diff})\) (mA) by Eq. (3), based on a calibration measurement with known Br2 concentrations described in the ESI.

\[ c(Br2)(aq)) = \frac{m \cdot I_{lim}(\text{diff})}{\bar{\nu}} \]

The calibration constant \(m = 0.00342466\) mol L\(^{-1}\) mA\(^{-1}\), while for Br2 concentrations the unit mol L\(^{-1}\) is applied. For different electrolytes depending on the chosen SoC, different Br2 concentrations are measured due to individual limiting currents.

2.4. [C2Py]Br concentration in the aqueous phase

Concentrations of [C2Py]Br in equilibrated aqueous solutions at SoC 0, 33, 60, 67, 70, 80, 90 and 100% and of further samples of aqueous phase in the bulk solutions during a cell test are detected with Raman spectroscopy at a Raman shift (\(\bar{\nu}\)) of \(\bar{\nu} = 1030 \, \text{cm}^{-1}\). At \(\bar{\nu} = 1030 \, \text{cm}^{-1}\) the excitation of the aromatic structure of the pyridine is given [50–52]. Calibration is done with 1.11 M [C2Py]Br in 7.7 M HBr solution. [C2Py]Br\(^{+}\)(aq) concentrations are calculated by comparing peak areas at \(\bar{\nu} = 1030 \, \text{cm}^{-1}\) of the measured solution with the 1.11 M [C2Py]Br solution (ESI).

2.5. Test cell setup

Cell tests are performed at \(\theta = 23\, {^\circ}\text{C} \pm 1\, {^\circ}\text{C}\) in a self-developed H2/Br2-RFB single cell with a geometric membrane area of 40 cm\(^2\). A scheme of the setup is shown in the ESI (Figure S-1). The positive half cell contains a graphite felt electrode embedded in a flow frame. Electrolyte is stored in a capped glass tank. Aqueous bromine/bromide electrolyte is pumped through the felt electrode with a constant flow rate of 30 mL min\(^{-1}\) and after Br2 concentration is determined in the ESI. The second fused salt phase stays in the tank and is not circulated. The current collectors’ material is Glassy Carbon. Used membrane electrolyte assemblies (MEA) are Nafion®117 membranes, based on PSSA membrane technology, including a single side catalyst coating of 3 mg Pt cm\(^{-2}\) on carbon. The catalyst is used for the hydrogen reactions in the negative half cell. A graphite plate, with self-milled meander structure and gas diffusion layer (GDL) for the gas side supply is used as current collector in the negative hydrogen half cell. The negative hydrogen half cell is operated in a flow through mode but non-recyclable with a stoichiometric factor (\(\lambda\)) of \(\lambda = 6.57\) and fed with dry H2 of 100 mL min\(^{-1}\) during cycling (Fig. 1/a). The parameters...
determined during the experiments are: Cell voltage \( E_{\text{Cell}} \neq 0 \) under load, redox potential \( \phi(\text{Br}_2/\text{Br}^-) \) versus the normal hydrogen electrode (NHE) and half cell potentials of the positive bromine half cell \( \phi(\text{Br}_2/\text{Br}^-) \neq 0 \) vs. NHE and the negative hydrogen half cell \( \phi(\text{H}^+/\text{H}_2) \neq 0 \) vs. NHE. A so-called “residual voltage”, \( \Delta E_{\text{RES}} \) is calculated from these values according to Eq. (4):

\[
\Delta E_{\text{RES}} = E_{\text{Cell}} + \phi(\text{Br}_2/\text{Br}^-) + \phi(\text{H}^+/\text{H}_2) - V
\]

(4)

It essentially reproduces the overvoltages between the positive and the negative half cell and represents the sum of electrolyte and membrane resistances. Qualitatively noticeable occurrences of cell voltage behaviour are determined from the galvanostatic cycle test. Investigation focuses on the bromine half cell. The measurement setup is shown in detail in the ESI.

2.6. Cycling tests in \( \text{H}_2/\text{Br}_2\)-RFB single cell

Galvanostatic cycling tests are performed at a current density of \( i = \pm 50 \text{ mA cm}^{-2} \) between the voltage thresholds of \( +1.55 \text{ V} \) and \(+0.20 \text{ V} \). The depth of discharge is determined by limiting the converted electrical charge during the experiment, as shown in Table 1. This results in maximum charge and discharge times for all cycle tests (Table 1). Two types of cell tests are carried out: For qualitative performance investigation (1) one test is performed starting in discharge operation mode from SoC 100% to 90% and back to 100%. After repeating this experiment for three times, the same procedure is applied to a depth of discharge from SoC 100% to 90% and back to 100%. In addition, for cycling durability (2), three tests starting from SoC 100% to SoC 80, 70 and 60% are investigated for 30 cycles each. The lower SoC threshold is defined as SoC 80, 70 and 60%. In this cell test also the mass loss of the bromine electrolyte is determined in parallel to the cycling threshold is defined as SoC 80, 70 and 60%. In this cell test also the mass loss of the bromine electrolyte is determined in parallel to the cycling performance. Therefore, lower quantities of Br are pumped into the positive half cell for discharge operation. Simultaneously, the concentration of \([\text{C2Py}]^+(aq)\) decreases, since these ions are transferred in the presence of polybromides into the fused salt according to Eq. (2). For SoC \( \geq 70\% \), no \([\text{C2Py}]^+(aq)\) is detected in the aqueous phase for electrolyte solutions in equilibrium. All \([\text{C2Py}]^+\) cations are transferred into the fused salt. Conductivities of the aqueous electrolyte (Table 2) increase between SoC 0 and 66%. The conductivity \( \kappa \) is high with \( \kappa > 350 \text{ mS cm}^{-1} \) and therefore suitable for use in redox flow batteries. For SoC \( \geq 66\% \) it decreases strongly due to decreasing proton concentration, shown in Ref. [12]. Protons are consumed by the cell reaction according to Eq. (1) during the charge process. The corresponding fused salt conductivity (Table 2) is with 51.6 \( \leq \kappa \leq 93.6 \text{ mS cm}^{-1} \) much lower compared to the conductivity of the aqueous phase. The result of \( \text{Br}_2(aq) \) and \([\text{C2Py}]^+(aq)\) concentration as well as conductivities of both phases are introduced here to validate results of the cell tests within the following chapters.

3.2. Stepwise cycling of the \( \text{H}_2/\text{Br}_2\)-RFB single cell

As a charge operation starting at SoC 0% is not possible (Section 3.1) an alternative approach to investigate cell cycling performance is applied: The cell is cycled within SoC steps, starting with galvanostatic discharge operation from SoC 100%, while step length is increased (SoC 100-90%, SoC 100-80%, SoC 100-70%, SoC 100-60%). From Section 3.1 it is known that the electrolyte is free of BCA at SoC 100%. Between each of these subsequent steps three galvanostatic cycles with constant charge/discharge times are operated with a current density of \( \pm 50 \text{ mA cm}^{-2} \). The results are depicted in Fig. 2.

In general, cycling of the cell with this electrolyte between SoC 100-90% and SoC 100-80% is possible without difficulties, while anomalies in the cell voltage already occur in the cycling range SoC 100-70%. Cycling below SoC 70% is not possible with this electrolyte, whereby the \([\text{BCA}]^-\) cations in the positive half cell are considered to be responsible for this limitation:

| SoC range for cycling | Converted electrical charge Q/ Ah L\(^{-1}\) | Charge, discharge time for \((i = \pm 50 \text{ mA cm}^{-2} \text{ and } V = 90 \text{ mL} / \text{h})\) |
|-----------------------|---------------------------------------------|--------------------------------------------------------------------------|
| SoC 100-80%           | 35.91                                       | 1.616                                                                    |
| SoC 100-70%           | 53.78                                       | 2.424                                                                    |
| SoC 100-60%           | 71.83                                       | 3.232                                                                    |
Table 2
Electrolyte properties of investigated electrolyte mixtures at specific SoCs for pure HBr/Br2/H2O electrolytes and electrolytes with [C2Py]Br as an additive: The concentration of Br2 in the aqueous phase of a BCA-free HBr/Br2/H2O electrolyte with linear rise over the SoC range is compared to the concentration of Br2 in the aqueous phase of the same electrolytes containing [C2Py]Br. For the electrolyte containing [C2Py]Br, the concentration of [C2Py]+ cations is investigated to show the sequestration process according to Eq. (2) and electrolyte conductivities of the aqueous phase (large) and the fused salt phase (low) are compared for this electrolyte for validation of results in the following cell tests.

| State of Charge | BCA-free HBr/Br2/H2O | [C2Py]Br electrolyte |
|-----------------|----------------------|----------------------|
|                 | Aqueous (aq)         | Aqueous (aq)         | Fused salt (fs) |
| SoC%            | Concentration of Br2 (aq)/M [a] | Concentration of Br2 (aq)/M [b] | Concentration of (C2Py)+ [c] | Conductivity (aq) at 23 °C ± 1 °C/m/s cm⁻¹ [b] | Conductivity (fs) at 23 °C ± 1 °C/m/s cm⁻¹ [b] |
| 0               | 0                    | 0                    | 1.110                  | 471.3                  | -                         |
| 33              | 1.12                 | 0.117                | 0.307                  | 652.8                  | 51.6                       |
| 60              | 2.01                 | 0.203                | 0.052                  | 710.2                  | 76.9                       |
| 66              | 2.23                 | 0.208                | 0.023                  | 694.0                  | 79.2                       |
| 70              | 2.34                 | 0.222                | 0 [c]                  | 686.4                  | 82.8                       |
| 80              | 2.68                 | 0.264                | 0 [c]                  | 619.8                  | 86.9                       |
| 90              | 3.11 [d]             | 0.259                | 0 [c]                  | 514.1                  | 91.8                       |
| 100             | 3.35 [d]             | 0.237                | 0 [c]                  | 363.4                  | 93.9                       |

[a] calculated, [b] measured, [c] values below detection limit and [d] total concentration of Br2 in sample, while for SoC 90% and SoC 100% in pure HBr/Br2/H2O a separate phase of pure Br2 is formed (ref. [12]).

Increasing overvoltages in the cell. As limitations of charge transfer resistance or the thermodynamic change of the cell voltage (redox potential Br2/Br2), as well as mass transport limitation in front of the electrodes can be excluded, possible overvoltages must be due to the ohmic resistances, attributed to the electrolyte resistance and the membrane resistance. This is confirmed from the residual voltage ΔE_{RES}, which primarily indicates the anomaly of the cell voltage and approximately represents the sum of electrolyte and membrane overvoltages. Both phenomena “A” and “B” are discussed further in Section 3.3 and 3.4.

A further discharge to SoC ≤70% is not possible, leading to a maximum useable electrolyte capacity of around 53.9 A h L⁻¹ which constitutes only 30% of the targeted capacity of 179.56 A h L⁻¹. The possible operating range for the cell is limited to the SoC range between SoC 100% and 70%, while from lower SoCs, the cell cannot be charged again.

During the experiment, the ohmic cell resistance (Fig. 2/b) increases with increasing cycle numbers and discharge depth, starting from 0.98 Ohm cm², with slowly rising resistance values for the first six cycles measured before and after discharge process (SoC 100-90% and SoC 100-80%). From the 7th cycle on (SoC 100-70%) the ohmic cell resistances after discharge are increased compared to the values before discharge. From the 10th cycle on the ohmic resistances increase strongly. Since the voltage peak during charging (Fig. 2/a – depicted by “A”) occurs reversibly during the charging process, a rise of cell resistance can be suggested by interaction of [C2Py]+(aq) in the aqueous solution with the membrane.

In order to investigate both phenomena “A” and “B” in cell voltages in detail, both, charge and discharge processes, are considered separately by examination of electrolyte samples and analysis of membrane samples in sections 3.3 and 3.4.

3.3. Investigation of the anomaly in voltage behaviour during the charge process

In order to study the phenomena in the positive half cell during the charge process marked with “A” in Fig. 2/a, a further cell test between SoC 100-60% is performed (Fig. 3/a) within the enlarged voltage threshold to 3.0 V, and showing again a strong voltage peak during charge operation. For the charge operation starting from SoC 60% at different times (Fig. 3/a), samples of the aqueous bulk solution in the electrolyte glass tank are collected and the concentration of [C2Py]+(aq) is examined by Raman spectroscopy. Raman spectra of [C2Py]+(aq) with a strong, single peak at $\bar{v} = 1030.2$ cm⁻¹ are obtained (Fig. 3/b). The concentration of [C2Py]+(aq) in aqueous phase decreases from 168
At the beginning of the charging process, the cell voltage rises sharply in the form of an ohmic overvoltage and after a certain time returns to expected values. At the same time (ii) the Raman measurements indicate, that [C2Py]+ (aq) cations are present in the aqueous electrolyte solution at the beginning of the charge process and their concentration decreases over time. Finally, (iii) with a certain time delay, viscous single droplets of fused salt flowing form the cell outlet into the tank are observed.

Therefore, the voltage peak during the charging process can be assigned to the formation and accumulation of fused salt [C2Py]Br_{2n+1} in the positive half cell and only occurs during charge operation (Eq. (2)). A prerequisite to form fused salt is the presence of dissolved [C2Py]+ (aq) cations in the aqueous phase and the formation of bromine in the positive half cell. During the preceding discharge process [C2Py]+ cations are released from the fused salt phase into the aqueous electrolyte phase and are available in tenth-molar scale, as it is shown in (Fig. 3/b and c) at t_1 = 0 min with c([C2Py]+) = 168 mM. Even for electrolytes at equilibrium between the phases, dissolved [C2Py]+ (aq) cations in the aqueous phase for SoC < 70% are present, as shown in Table 2. In general during discharge process higher amounts of [C2Py]+ (aq) cations are released from the fused salt phase into the aqueous phase, compared to [C2Py]+ (aq) concentrations in equilibrium (Fig. 3/b).

During the charge process, bromide is oxidized at the electrode surface of the positive half cell and released into the aqueous electrolyte in the form of polybromides. If, however, [C2Py]+ (aq) cations are present, the resulting hardly soluble [C2Py]-polybromide salts, form the liquid fused salt, and clog the porous felt. Electrolytic conductivities of the fused salt phase are examined, shown and compared with the conductivities of the aqueous electrolyte solutions in Table 2. Conductivities of the fused salt of [C2Py]Br_{2n+1} over the SoC range between 33% and 100% give values between 51.6 and 93.9 mS cm⁻¹, while the aqueous solution reaches conductivities from 363.4 mS cm⁻¹ to 694.0 mS cm⁻¹ (Table 2). Conductivities are 3.9-6.6 times larger for aqueous solution compared to the fused salt. The low electrolyte conductivity of fused salt leads to high overvoltages compared to the application of the pure aqueous phase. Since both half cell potentials do not follow the increasing trend of cell voltage, there is no increasing kinetic or mass transport inhibition neither in the positive nor the negative half cell (see Fig. 3/a) connected to the observed phenomenon.

In addition to the fact of the formation of a fused salt phase in the porous electrode, it is observed that the effect of the fused salt formation is reversible. During charge, Br₂ is constantly generated at the rate of +0.037 mol s⁻¹ in the positive half cell caused by galvanostatic charging with a current density of +50 mA cm⁻², which can be calculated from Faraday law. The [C2Py]+ (aq) cations are present in the solution to a limited extent and their concentration decreases as charging progresses (Fig. 3/c) by formation of fused salt. As a consequence, over the time, less amounts of [C2Py]+ cations and of fused salt are formed until complete depletion of [C2Py]+ (aq). In parallel, due to the slow outflow of the fused salt from the positive half cell, the cell voltage decreases, while the clogged pores in the felt electrode are refilled with aqueous electrolyte. The overvoltage in the cell stagnates by peaking and then decreases until it changes into the expected curve of the cell voltage.

3.4. Rise of ohmic resistance during discharge operation

After investigating the anomaly occurring during the charging process, a subsequent task is to investigate the increasing overvoltage during the discharging process, found in Section 3.2. A rise of the ohmic cell resistance shown in Fig. 2/a, marked by “B” can only be attributed to the electrolyte conductivity or the membrane conductivity during discharge as mentioned in Section 3.2 and is investigated further here.

Ionic conductivity of the aqueous electrolyte (Table 2) is not the reason for this ohmic cell resistance: During the discharge process from SoC 100 to 60%, the conductivity increases from 363.4 to 710.2 mS
Fig. 3. Investigation of the processes in the bromine half cell during the charge process in (a) occurring voltage peak between SoC 100-60% by sampling of aqueous bulk electrolyte at the times t₁ to t₆. Samples are analysed by (b) Raman spectroscopy for the presence of [C2Py]⁺ cations in aqueous solution at \( \tilde{v} = 1030.2 \text{ cm}^{-1} \) and (c) plotting the present [C2Py]⁺ (aq) concentrations as a function of time t and comparing them with [C2Py]⁺ (aq) concentrations at equilibrium on the time scale. [C2Py]⁺ (aq) concentrations at equilibrium in (c) are transferred from Table 2 and their position in the diagram is converted to the time scale, as the electrolyte holds a specific SoC for each individual time.
cm\(^{-1}\), as the concentration of conductive protons in the polysulfate rise\[12\] during discharge operation.

To investigate this contradiction, the influence of the BCA-containing electrolyte on the membrane functionality is investigated further. The conductivity of perfluorosulfonic acid (PFSA) membranes depends on their saturation with water. 16 water molecules per sulfonate group in the membrane result in a maximum membrane conductivity\[59\]. To determine the influence of [C2Py]\(^+\)(aq) ions on membrane conductivity, membrane samples are placed in aqueous electrolyte samples with and without [C2Py]\(^+\)(aq) for SoC 0, 33, 60, 70, 80, 90 and 100% ex situ and are examined by FT-IR spectroscopy shown in Fig. 4.

FT-IR measurements show infrared absorption bands of Nafion (Fig. 4) with assigned wavenumbers at \(\tilde{\nu} = 1198\) cm\(^{-1}\) for symmetric CF\(_2\) stretching\[60-62\] and \(\tilde{\nu} = 1143\) cm\(^{-1}\) for asymmetric CF\(_2\) stretching\[62-64\] of the PTFE backbone in the Nafion 117 membrane. At \(\tilde{\nu} = 1302\) cm\(^{-1}\) the C-C stretching of the backbone is visible\[62\]. Characteristic peaks of the side chain are visible at \(\tilde{\nu} = 982\) cm\(^{-1}\) for the symmetric C-F stretching in CF\(_2\)-CF-R-CF\(_3\) group\[62,63,65-67\] and at \(\tilde{\nu} = 969\) cm\(^{-1}\) for C-O-C stretching\[62,63,65,67\]. A shoulder at \(\tilde{\nu} = 1126\) cm\(^{-1}\) shows the asymmetric S=O oscillation of the sulfonates\[62\]. All peaks are known from literature and do not show any FT-IR shift due to treatment with different electrolytes except for the peak at \(\tilde{\nu} = 1056\) cm\(^{-1}\). The peak with a FT-IR shift of \(\tilde{\nu} = 1056-1060\) cm\(^{-1}\) is the symmetrical stretching of the S-O molecular oscillation in the sulfonate group of the side chain in the PFSA\[61,66,67\].

Depending on the SoC of the electrolyte, rising concentration of [C2Py]\(^+\)(aq) leads to rising interaction with the sulfonate membrane, causing a higher ohmic overvoltage of the membrane: The peak wavenumber at \(\tilde{\nu} = 1056-1060\) cm\(^{-1}\) decreases with decreasing SoC, as shown in Fig. 4 with a red arrow. The shift of this S-O oscillation peak is compared in Table 3 to the shift of the peak of the S-O oscillation of a membrane treated in BCA-free HBr/Br\(_2\)/H\(_2\)O electrolytes and correlates identically with the increasing concentrations of [C2Py]\(^+\)(aq) in the aqueous electrolyte solution from Table 2. Rising [C2Py]\(^+\) concentrations cause a stronger shift of the S-O peaks downwards to \(\tilde{\nu} = 1051.3\) cm\(^{-1}\). Hugo et al.\[68\] describe rising membrane resistances in ex situ investigations of membranes, but without showing quantitative correlation between membrane resistance and actual [BCA]\(^+\) concentration. The interaction of the cation with the sulfonate group is a cation exchange reaction\[69\]. The organic cation [C2Py]\(^+\) forms with the sulfonate a contact pair, while [C2Py]\(^+\) has a large radius compared to protons and the hydrophobic character of the cation reduces the polarity of the environment. The shift of the S-O peak to lower FT-IR shifts is an effect of the weaker ion pair dipole of the S-O group by the contact pair SO\(_3\).[C2Py]\(^+\)\[70\].

During discharge of the electrolyte [C2Py]\(^+\) is released from the fused salt in higher concentrations than in equilibrated electrolyte samples (Fig. 3/c), which is expected to intensify this effect.

The two effects triggered by the organic BCA cation limiting half-cell and membrane performance have been discussed in detail. Both effects are due to the presence of BCA cations. As a precautionary approach, the performance of the bromine half cell should be improved by avoiding the presence of quaternary ammonium cations. The influence of the investigated electrolytes on the long-term cycle ability of the battery is now to be investigated further.

3.5. Cycle performance and durability over 30 cycles

In previous cell tests, only three cycles have been performed for each cycling SoC range to investigate upcoming phenomena related to the BCA. This results in a temporal snapshot for each SoC range. Based on the results from the previous cell test, this section describes cycling tests of 30 cycles per observation area for SoC 100-80%, SoC 100-70% and SoC 100-60% to investigate long-term performance of the cell and electrolyte. All tests are carried out starting with a discharge process of an electrolyte at SoC 100%.

![Absorption units vs Wavenumber](image-url)

**Fig. 4.** FT-IR spectra on Nafion 117 membranes with pretreatment in aqueous electrolyte samples with and without [C2Py]Br at SoC 100, 90, 80, 70, 60, 33 and 0%. Membrane treated in BCA-free HBr/Br\(_2\)/H\(_2\)O without containing [C2Py]\(^+\)(aq) are used as reference membranes. In the embedded diagram the shift of the FT-IR peak for symmetrical stretching oscillation S-O of the sulfonate group is highlighted. The red arrow shows peak shift from N117 without [C2Py]\(^+\) electrolyte treatment via electrolytes containing [C2Py]\(^+\)(aq) at SoC 100% to SoC 0% with falling wavenumbers. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
3.5.1. Voltage characteristics and occurrence of BCA influence

Cell voltages and mass losses of the electrolyte over the number of cycles for tests between SoC 100-80% and 100-60% are measured and shown in Fig. 5. For the purpose of clarity, measurement results for cycling between SoC 100-70% are presented in the ESI (Figure S-2).

For cycling between SoC 100-80%, Fig. 5/a shows a voltage behaviour unaffected by [C2Py]+ cations, neither in the form of additional peaks during charge, nor an increased ohmic overvoltage during discharge. Cell voltage tends to decrease slightly. A similar performance for the test between SoC 100-70% can be observed shown in the ESI (Figure S-2). For the cycling test between SoC 100-60% (Fig. 5/b) instead, (i) voltage peaks described in Section 3.3, are formed from the 16th cycle during charge operation and (ii) towards the end of the discharge process the cell voltages progressively decrease for all cycles. While for the first 15 cycles only minor influence of [C2Py]+ on the cell performance is visible, from cycle 16 onwards [C2Py]+ cations in aqueous electrolytes cause performance losses. Effects and dependency on the number of cycles is discussed in the following subchapters.

While cycling between SoC 100-60% has not been possible in the preceding experiment for only three cycles (Section 3.2) due to overvoltages, in the long term test it is feasible during the initial 15 cycles. While during the experiment here in Section 3.5 the fused salt reposes in the glass tank and only the aqueous phase is pumped through the cell, during stepwise cycling in Section 3.2 the mixture of fused salt and aqueous phase has been slightly stirred in the glass tank. By stirring, higher amounts of [C2Py]+ are transferred from fused salt to the aqueous phase and lower the cell performance as shown in the experiment in Section 3.3. In addition, the upper cell voltage threshold is enlarged to 3.0 V.

3.5.2. Characteristics of posolyte mass loss by crossover through membrane

In order to maintain the capacity of the battery, the entire amount of electrolyte must be permanently available over the number of cycles. However, crossover can limit the useable capacity. A crossover of the electrolyte across the membrane is measured by the mass change of the posolyte in the tank and is shown in Fig. 5 + ESI Figure S-2 and a strong crossover for all tests is identified. The posolyte mass decreases for all tests sharply over the number of cycles. For cycling between SoC 100-80% posolyte mass loss of approximately 50 g (−33.9 wt%) within 100 h, for SoC 100-70% a loss of 60 g (−40.6 wt%) within 148 h and for SoC 100-60% a mass loss of about 52 g (−35.3 wt%) within 180 h are registered.

A clear, but strongly acidic liquid is collected in a wash bottle at the outlet of the hydrogen half cell for each test. The acidic character is received from HBr. In combination with the mass loss, this indicates a strong crossover of water, HBr and Br2 from positive to negative half cell during cycling. As Br2 is reduced with H2 to HBr at the platinum particles of the hydrogen half cell by catalytic reaction [3], a distinction between passing HBr and Br2 from mass loss is not feasible.

The sawtooth-shaped trend of the mass change is related to the storage of Br2 in the fused salt. During charging operation, Br2 is transferred to the heavy fused salt in the tank and the electrolyte mass in the tank rises, while the mass of the tank is recorded. In parallel the lighter aqueous phase is circulated. For the discharge process, Br2 enters into the aqueous phase and is stored after reaction as HBr in aqueous phase. The mass in the tank decreases.

3.5.3. Influence of electrolyte crossover on cell voltage for 30 cycles

Crossover of reactants and water influences the cell voltage during operation as well as the open circuit voltage. Average charge and discharge cell voltages of cycling tests are calculated from cell voltages and presented in combination with open circuit voltage in Fig. 6 to focus on durability of cell voltages. Average cell voltages for the SoC 100-80% cycle range slightly decrease for charge from 1.10 V to 1.02 V and for discharge from 0.87 V to 0.78 V. This trend appears more intense during cycling between SoC 100-70% for charge from 1.09 V to 0.95 V and especially during discharge from 0.85 V to 0.66 V. As for tests in the range of SoC 100-60% an influence of [C2Py]+ is obvious, cell voltages of this experiment are discussed in Chapter 3.5.4, while here the focus shall be on the effect of crossover of the active species HBr and Br2 on the cell voltage. Also open cell voltages (Fig. 6/b) show a trend for decreasing cell voltages. Charge and discharge voltages, open-circuit voltages (Fig. 6) as well as mass of the posolyte decrease with rising number of cycles. All changes indicate a change in electrolyte composition. Due to the crossover of Br2 in relation to the amount of HBr becomes lower in the electrolyte during cycling, leading to lower redox potentials according to Nernst equation and cell voltages over the cycle number for SoC 100-80% and SoC 100-70%. The development of the potentials base on concentration changes of the redox couple [49,72]: If predominantly (i) water from the positive half cell enters the negative half cell, the dissolved bromide and Br2 in the posolyte get increasingly concentrated. A concentration increase of HBr causes a strong increase in its activity coefficient [72,73] and so its activity. According to Nernst equation, the redox potential of the Br2/Br− and thus the cell voltage both decrease [72]. In parallel (ii) an increased crossover of Br2 compared to bromide ions from the posolyte through the membrane to the negative half cell leads to the same trend of decreasing cell voltage and open circuit voltage. Both processes (i) and (ii) happen in parallel, are caused by crossover through the membrane and intensify a limited energy output from the battery for rising number of cycles.

3.5.4. Influence of [C2Py]+ cations on cell voltages for 30 cycles

For cycling between SoC 100-60% from cycle 16 onwards, increasing cell voltage peaks during the charge process and strongly decreasing voltages towards the end of discharge process are recognized (Fig. 5). The mean charge voltage increases strongly to values > 1.2 V (Fig. 6/a), while over the entire cycle range the mean discharge voltage decreases with a pronounced distance from further experiments (e.g. SoC 100-80%) down to 0.57 V. Anomalies caused by the formation of fused salt in the positive half cell during the charging process and the increasing resistance of the Nafion membrane in contact with [C2Py]+ (aq) are intensified with number of cycles onwards.

The crossover of Br2 leads due to the release of [C2Py]+ from the fused salt phase in the aqueous phase to a reduced performance in the range SoC 100-60% for both discharge and charge operation. (Concentrations of [C2Py]+ have not been measured here.) This tendency is caused by an increasing concentration of [C2Py]Br in the aqueous solution with the number of cycles: Crossover of Br2 from the positive to the negative half cell causes decreasing Br2 concentration in the posolyte during cycling. In order to retain the chemical equilibrium of Br2 between the aqueous phase and the fused salt in the tank, this lack of Br2 leads to a transfer of Br2 from the fused salt into the aqueous electrolyte. Following Eq. (2), thereby [C2Py]+ is released in the aqueous phase too. During the first 15 cycles this process does not occur or is not visible.

| Table 3
| FT-IR shift of νsym(S–O) of FT-IR absorption for Nafion N117. |
| νsym(S–O) of -SO3 group at different N117 samples soaked with different aqueous electrolytes HBr/Br2/H2O including [C2Py]Br and HBr/Br2/H2O pure |
| SoC 0% | SoC 33% | SoC 60% | SoC 70% | SoC 80% | SoC 90% | SoC 100% |
| 2051.27 | 2053.20 | 2054.17 | 2053.92 | 2055.13 | 2055.37 | 2055.61 | 1055.61 |
From cycle 16 on, \([\text{C2Py}]^+\) is progressively released into the aqueous phase, pumped into the cell and reduces performance for rising number of cycles.

3.5.5. Durability of membrane performance

To determine membrane performance durability for 30 cycles, ohmic cell resistances before and after each discharge step are determined by EIS and shown in Fig. 7. All cells filled with posolyte at SoC 100% showed before the first discharge different cell resistances between 1.17 and 1.43 Ohm cm\(^2\). The ohmic cell resistances before the first discharge depend on the cell setup and are not reproducible for this cell. Regardless of this resistances, clear trends in the ohmic cell resistances...
Fig. 6. Cell voltages depending on the operation mode: (a) Average charge (square) and discharge (dot) cell voltages per cycle from the cycle tests for the examined SoC ranges (SoC 100-80% - red, SoC 100-70% - blue, SoC 100-60% - purple) at galvanostatic operation mode with $i = \pm 50 \text{ mA cm}^{-2}$, as well as (b) open circuit voltages before discharge process (square) and after the discharge process (dot) per cycle for the examined SoC ranges (SoC 100-80% - red, SoC 100-70% - blue, SoC 100-60% - purple). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
as a function of the number of cycles and depth of discharge are observed and can be separated in two parts, depending of BCA-free aqueous electrolyte phases and BCA-containing aqueous electrolyte phases:

First (i) the ohmic cell resistances are approximately constant in the SoC 100-80% experiment, within a range of 1.48–1.70 Ohm cm$^2$ for 30 cycles and for cycling between SoC 100-70% for the first 15 cycles in the range of 1.29–1.31 Ohm cm$^2$. [C2Py]$^+$ (aq) cations are completely bound in the fused salt and have no effect on the membrane conductivity and on the cell voltages. For both tests a slightly higher resistance before discharge than after discharge operation for each cycle is observed. This differences depend on the conductivity of the aqueous electrolyte with a higher conductivity of 619.4 mS cm$^2$ at SoC 80% than 363.4 mS cm$^2$ at SoC 100%.

For (ii) cycling between SoC 100-70% from cycle 16 onwards, there is an increase in cell resistance after discharge, but a constant lower cell resistance before discharge (Fig. 7). For the cycle experiment SoC 100-60% a continuously increasing ohmic cell resistance after discharging as well as before discharging up to large values of >3.2 Ohm cm$^2$ is shown depending on the cycle number. Again, the rising amounts of [C2Py]$^+$ (aq) released from the fused salt with number of cycles onwards lead to rising membrane resistances. In addition, the increase in membrane resistance for the test between SoC 100-60% is irreversible compared to cycling between SoC 100-70%. Membrane resistance before and after discharge for cycling between SoC 100-60% have similar values within one cycle, even if [C2Py]$^+$ concentrations in the aqueous posolyte decrease during charge. The interaction between the cation and the membrane is an irreversible process, at least during regular cell cycling.

3.5.6. Cycling efficiencies

Cycling efficiencies are calculated from cell voltage and cell currents for each cycle by application of Eq. S-10 to S-12 (ESI) to evaluate and discuss performance stabilities. A CE of 100% is achieved for all cycles, caused by chosen experimental parameters with limited discharge depth. This CE results in EE and VE having equal values for the respective cycle (Fig. 8). During the last four cycles (27–30) for cycling between SoC 100-60%, discharge operation down to SoC 60% is limited by reaching the cell lower voltage threshold. The SoC of the electrolyte increases from SoC 60%–67% after discharge as depicted in Fig. 8.

If the cell is cycled in the range between SoC 100-80%, EE remains almost constant between 79.5 and 76.0% for 30 cycles (Fig. 8). Here, EE is mainly influenced by the conductivity of cell materials and the aqueous, BCA-free electrolyte. For the cycling between SoC 100-70%, a slight decrease in EE (EE = 69.8% for cycle 30) occurs from the 18th cycle onwards. If the cell is cycled between SoC 100-60%, the EE decreases continuously from EE = 73.5% (cycle 1) to EE = 37.1% (cycle 27). For cycling between SoC 100-70% and SoC 100-60% increasing [C2Py]$^+$ concentrations in aqueous solution over the number of cycles cause formation of fused salt and low membrane conductivity and lead to a strong decrease of EE.

4. Conclusion

The influence of BCA cations on the performance of the bromine half cell and a cell with a PFSA membrane was investigated using 1-ethylpyridin-1-ium bromide [C2Py]Br as an exemplary BCA. Here, [C2Py]$^+$ cations are present in aqueous solution in the electrolyte and bind Br$_2$ in form of polybromides in a second fused salt phase. However, [C2Py]$^+$ cations remain in the aqueous solution and are found to have the
following adverse effects on the cell performance:

1. During charge, Br\(_2\) and \([\text{C2Py}]^+\) cations are present in the positive half cell and form a fused salt \([\text{C2Py}]\text{Br}_{2n+1}\). Low conductivities of the fused salt in the electrode felt lead to an increase in overvoltage until all cations are bound in the fused salt in the electrode. Therefore, pumping of highly concentrated fused salt through the positive porous electrode is hence not recommended. The phenomenon is reversible and no longer present at the end of the charging process.

2. During discharge, \([\text{C2Py}]^+\) cations are released from the fused salt phase into the aqueous phase and interact with the sulfonate groups of the PFSA membrane, resulting in a lower membrane conductivity. With rising cycle numbers increasing concentrations of \([\text{C2Py}]^+(\text{aq})\) in the aqueous electrolyte phase lead to increasing membrane resistances. The process is mostly irreversible during cell test.

3. Over a longer cycling time, effects of crossover become apparent. In addition to water and HBr, there is increased Br\(_2\) crossover, which leads to lower cell voltages during operation. The depletion of Br\(_2\) in aqueous solution stimulates the release of Br\(_2\) and \([\text{C2Py}]^+\) from the fused salt phase to keep both phases equilibrated. Over the number of cycles, rising \([\text{C2Py}]^+(\text{aq})\) concentrations in the aqueous phase strongly promote the two effects mentioned above in (1) and (2).

\([\text{C2Py}]^+\) dissolved in the aqueous electrolyte results in a reduced usability of the available electrolyte capacity to a maximum 53.9 A h L\(^{-1}\) or 30% of the theoretical capacity (179.6 A h L\(^{-1}\)). Applying the measured average discharge cell voltage of 0.77 V in this capacity range a useable energy density of 41.5 Wh L\(^{-1}\) is achieved from experiments. The performance characteristics are quite limited. Further solutions must be developed to prevent this problem. First and foremost, the focus here should be on avoiding \([\text{C2Py}]^+\) cations in the aqueous electrolyte solution in the bromine half cell. Compared to vanadium electrolytes, these electrolytes are indeed competitive and a high degree of safety is ensured by the BCA.

**Credit author statement**

Michael Küttinger: Conceptualization, Methodology, Investigation, Data analysis, Visualisation, Writing – Original Draft, Writing – Editing and Review, Supervision, Resources. Ruben Bruntau: Methodology, Investigation, Data analysis, Visualisation, Writing – Editing and Review. Jakub K. Włodarczyk: Data analysis, Visualisation, Writing – Editing and Review. Peter Fischer: Writing – Review. Jens Tübke: Funding acquisition.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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