Electronic supplementary information (ESI)

to the manuscript “High energy density electrolytes for H₂/Br₂ redox flow batteries, their polybromide composition and influence on battery cycling limits” by Michael Küttinger, Jakub K. Włodarczyk, Daniela Daubner, Peter Fischer and Jens Tübke.

In the ESI the reader will find detailed information on the measurement methods used, parameter settings for measurements, chemicals and purities as well as evaluation steps. In addition, Raman results on aqueous HBr/Br₂/H₂O electrolytes are shown in figures and tables.

Experimental and methods

Chemicals
All analysed electrolytes are composed of distilled water (PURELAB Ultra Analytic/Veolia-ELGA), hydrobromic acid HBr 48 wt% (Alpha Aesar, 48 wt%) and elemental bromine Br₂ (Alpha Aesar, +98 wt%).

Electrolyte preparation
For this electrolyte investigation an aqueous 7.7 M HBr solution is the initial electrolyte solution. A lower concentration compared to commercially available hydrobromic acid (HBr 48 wt%) with a difference of around 1.1 M is used, to allow the replication of other dilutions. Charging and discharging are theoretically possible between 7.7 M HBr and 0 M HBr. This range is evaluated with 24 samples, with a concentration change of Δc(HBr) = -0.335 M and Δc(Br₂) = 0.167 M per sample. The correlation between Δc(HBr) and Δc(Br₂) is stoichiometric and represented by eq. 1. The volume (V) of each sample is V = 10 mL. Concentrations of HBr and Br₂ in solution are shown in table 2 in the main manuscript. Each sample is used for the investigation of (i) electrolytic conductivity of the solution, (ii) detection of a possible miscibility gap of the solutions and (iii) Raman investigations for polybromide detection as a basis for the calculation of polybromide concentrations and equilibrium constants of the polybromide equilibria according to equations 4 and 5 (main manuscript). In addition to HBr/Br₂/H₂O samples described above, samples without Br₂ based on HBr/H₂O are mixed in order to investigate reference conductivities of pure HBr/H₂O electrolytes and compare them with solutions including Br₂. 24 samples are prepared with a volume of V = 10 mL and a concentration change of Δc(HBr) = -0.335 M in aqueous solution. For all samples, the amount of water is constant starting from a solution with c(HBr) = 7.7 M corresponding to the theoretical conditions in a positive bromine half-cell of a H₂/Br₂-RFB. For a cell test, V = 60 mL of discharged electrolyte with c(HBr) = 7.7 M HBr in H₂O was prepared.

Cycling cell test
A cell test is performed with a test cell developed at Fraunhofer ICT. As membrane electrolyte assembly (MEA) a Nafion 117 membrane with single sided Pt/C catalyst loading (3 mg Pt cm⁻²) from Baltic Fuel Cells (Germany) is used as hydrogen half-cell catalyst. The membrane has a geometrically active surface area of 40 cm². The gas diffusion electrode of the negative hydrogen half-cell consists of a gas diffusion layer (GDL) BC29 from SGL Carbon (Germany) and a current collector FU 4369 from Schunk Kohlenstofftechnik (Germany) with a milled meander structure to supply the gas anode with hydrogen and to remove formed hydrogen and water. The anode side is continuously fed with hydrogen from a gas cylinder with 100 mL min⁻¹ at 1.013 bar or higher, leading to stoichiometric factor λ ≥ 1.31. There is 31 % more hydrogen available compared to the amount needed during discharge. The hydrogen produced during the charging process is not stored. No external humidification of the hydrogen is applied during the measurements.

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manuscript). On one hand, the redox potential of the cathode at the GC rod versus Hg/Hg$_2$SO$_4$/K$_2$SO$_4$(sat.) is measured. On the other hand the half-cell potential $\phi$(Br$_2$/Br$^-$)$_{redox}$ during charge and discharge operation of the bromine half-cell connected via the electrolyte in the tube against Hg/Hg$_2$SO$_4$/K$_2$SO$_4$(sat.) is measured, according to figure 2 in the main manuscript. The negative hydrogen half-cell contains a dynamic hydrogen electrode (DHE) according to 1 to determine the potential of the hydrogen anode. The cell voltage $E_{cell}$ at under load, the redox potential $\phi$(Br$_2$/Br$^-$)$_{redox}$ versus a Hg/Hg$_2$SO$_4$/K$_2$SO$_4$(sat.) and half-cell potentials of the positive bromine half-cell $\phi$(Br$_2$/Br$^-$)$_{redox}$ vs. the normal hydrogen electrode (NHE) and the negative hydrogen half-cell $\phi$(H$^+$/H$_2$)$_{redox}$ vs. NHE were determined in parallel during cycling experiments. A so-called "residual potential" $\Delta E_{Res}$ is calculated from these values according to eq. 1:

$$\Delta E_{Res} = E_{Cell} - \phi_{(Br_2/Br^-)_{red}} - \phi_{(H^+/H_2)_{red}}$$

(1)

It essentially reproduces the overvoltages between the anode and cathode, and represents the sum of electrolyte resistance and membrane resistance. Kinetic inhibitions and mass transport limitation at the electrodes are represented by the half-cell potentials. Qualitative noticeable occurrences of cell voltage behaviour are determined from the galvanostatic cycle test of a test cell.

The measurement setup is shown in figure 2 in the manuscript including all voltage and potential measurements.

Investigation of the miscibility

24 electrolyte samples are prepared with the limiting concentrations of 7.7 M HBr/0 M Br$_2$ and 0 M HBr/3.85 M Br$_2$. The samples are examined by visual inspection at $\theta = 23$ °C for any phase separation of the aqueous phase and a non-soluble bromine phase. The glass vials are observed from below against a light source and drops or a complete coating of the vials’ bottom with a non-transparent deep brown bromine phase are used as a criterion for a miscibility gap.

Conductivity of electrolyte solutions

Electrolytic conductivities are measured for all 48 samples between the concentration limits at $\theta = 23$ °C using an LF1101 conductivity cell (SI Analytics/Germany). Electrolytes with HBr/Br$_2$/H$_2$O, and electrolytes without Br$_2$ in solution are examined. Ohmic resistances of the electrolytes $R_{Electrolyte}$ are measured by potentiostatic impedance spectroscopy with an excitation of $\dot{u} = 10$ mV (amplitude) in the frequency range between 1 MHz and 100 Hz at a potential offset of 0 mV and converted into electrolytic conductivities $\kappa$ according to eq. 3. The cell constant $K_{Conductometer}$ of the conductivity cell is determined using 1 M KCl solution and a known conductivity of 303.9 mS cm$^{-1}$ at $\theta = 23$ °C (determined by linear regression for $\theta = 23$ °C from 2 (eq. 2):

$$K_{Conductometer} = \frac{1}{R_{1M\,KCl\,t=23\,^\circ C}/K_{1M\,KCl\,t=23\,^\circ C}} \quad \text{[K] = cm}$$

(2)

$$K_{Electrolyte, \, t=23\,^\circ C} = \frac{1}{R_{Electrolyte, \, t=23\,^\circ C} \cdot K_{Conductometer}} \quad \text{[K] = S cm}^{-1}$$

(3)

Ohmic resistances from the conductivity measurement $R_{Electrolyte}$ were corrected by the ohmic resistance of the cables and connections. Based on the miscibility gap and the measured electrolyte conductivities, an applicable operating range is defined in terms of states of charge (SOC) from 0 % to 100 % in the results chapter "Definition of the operating range for HBr/Br$_2$ electrolytes".

Solubility of Br$_2$ in HBr solutions

The solubility curve of bromine in HBr solutions is determined by preparing aqueous HBr solutions of different concentrations c (HBr) between 0 M HBr and 5 M HBr (0, 0.1, 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5 M HBr) at room temperature $\theta = 23$ °C. Bromine is added dropwise with a pipette. Each drop of Br$_2$ weighs approximately 25 mg. The total mass of the sample and the change in mass due to the addition of bromine are determined gravimetrically. After adding bromine, the solution is shaken vigorously and left to dissolve completely. If no drop of liquid and heavy bromine remains undissolved in the sample, the solution is not yet saturated with bromine. This procedure is continued iteratively until a drop of bromine remains in the sample. If one drop of bromine remains the sample is saturated with bromine. This can be recognized as a deep brown separate drop which collects at the bottom of the sample due to the high density (ρ) of bromine $\rho = 3.1028$ g cm$^{-3}$ at $\theta = 25$ °C. The addition of bromine increases the...
volume and mass of the sample solution. In order to determine the actually existing concentrations at saturation of $c(\text{HBr})_{\text{sat}}$ and $c(\text{Br}_2)_{\text{sat}}$, the volume and mass of the samples in the saturated state $V_{\text{sat}}$ and $m_{\text{sat}}$ are measured. The total volume $V_{\text{sat}}$ of the solution is determined volumetrically and the total mass of the sample $m_{\text{sat}}$ gravimetrically. By increasing the volume, the concentrations in solution are reduced and can be calculated according to eq. 4 and eq. 5:

$$c(\text{HBr})_{\text{sat}} = \frac{c(\text{HBr})_0 V_0}{V_{\text{sat}}} \quad \text{eq. 4}$$

$$c(\text{Br}_2)_{\text{sat}} = \frac{m_{\text{sat}} - m_0}{M_{\text{Br}_2 V_{\text{sat}}} \text{ eq. 5}}$$

$V_0$ is the volume of the initial HBr solution with the initial concentration $c(\text{HBr})_0$ and its mass $m_0$. The molar mass of Br$_2$ is represented by use of $M_{\text{Br}_2}$. The solubility curve of the aqueous HBr/Br$_2$ electrolytes is obtained by plotting the saturation concentration $c(\text{Br}_2)_{\text{sat}}$ versus the saturation concentration $c(\text{HBr})_{\text{sat}}$.

**Polybromide determination and polybromide distribution by Raman analysis**

By means of Raman spectroscopy on the electrolyte samples, the occurrence of the different polybromides Br$_3^-$, Br$_5^-$, etc. in aqueous solution in the prepared samples of HBr/Br$_2$/H$_2$O is investigated. Raman spectra are measured with the HORIBA LabRAM HR spectrometer (JOBIN YVON Technology GmbH, Germany) at room temperature $\theta = 23 \degree$ C in the wavenumber ($\nu$) range from $\nu = 50$ cm$^{-1}$ to 4000 cm$^{-1}$. A frequency-doubled Nd:YAG laser (neodymium-doped yttrium-aluminium-garnet laser) with an excitation wavelength of $\lambda = 532$ nm (green) is used as laser source and a charge coupled device camera detector (CCD) is used at $\theta = -70 \degree$ C. Electrolyte samples are pipetted into a quartz glass cuvette (Suprasil Q5, Helma), sealed and examined under the microscope. The focal point is positioned just below the edge of the front glass of the cuvette and the position of the carrier table is fixed to obtain reproducible Raman spectra. For all samples and wavenumbers, the exposure time is 10 s and the number of repetitions per sample for calculating the average is set to three.

**Simulation of the electrolyte composition**

To investigate the validity of polybromide equilibria and equilibrium constants from literature at high reactant concentrations, concentrations of polybromides, HBr and Br$_2$ in equilibrium are simulated. The corresponding concentrations of Br$_2$, tribromide and pentabromide ions are calculated for a selected range between 0 M and 7.7 M HBr. To determine global concentrations of Br$_2$ $c(\text{Br}_2)_T$, the stoichiometric relationship, including the global HBr concentration $c(\text{HBr})$, and its concentration $c(\text{HBr})_0 = 7.7$ M, becomes relevant:

$$c(\text{Br}_2)_T = \frac{c(\text{HBr})_0}{2} \left(1 - \frac{c(\text{HBr})_0}{c(\text{HBr})_0/M} \right) = 3.85 \text{ M} \left(1 - \frac{c(\text{HBr})_0}{7.7 \text{ M}} \right) \quad \text{eq. 6}$$

The concentrations for $c(\text{Br}_3)_\text{eq}$, $c(\text{Br}_5)_\text{eq}$, $c(\text{Br}_2)_\text{eq}$ and $c(\text{HBr})_\text{eq}$ in equilibrium are calculated using eq. 4 and 5 of the main article ($K_3$ and $K_5$) with $K_3 = 16$ L mol$^{-1}$ and $K_5 = 37$ L$^2$ mol$^{-2}$ for individual operating SOC points in each case iteratively including eq. 7.

$$c(\text{HBr})_\text{eq} = c(\text{HBr})_T - c(\text{Br}_3)_\text{eq} - c(\text{Br}_5)_\text{eq} \quad \text{eq. 7}$$

The operating points are defined by the state of charge (SOC) of the electrolyte. The SOC range will be defined in chapter “Definition of the operating range for HBr/Br$_2$ electrolytes”. Concentrations are plotted as a function of SOC in chapters “Theoretical concentrations and polybromide equilibria” and “Polybromide distribution and polybromide concentration verification of polybromide equilibria” both in the main manuscript.
Results of investigation on HBr/Br₂/H₂O electrolytes by helps of Raman spectroscopy

Raman spectra of HBr/Br₂/H₂O electrolytes

![Raman spectra of HBr/Br₂/H₂O electrolytes](image1)

Figure S1: Raman spectra of different HBr/Br₂/H₂O electrolytes depending on the state of charge SOC (SOC 0 % to SOC 115 %), shown for a Raman shifts between \( \tilde{\nu} = 100 \) and 350 cm\(^{-1}\). Selected range for Raman shifts exclusively depicts Raman bands for polybromides and bromine. Mixing conditions of the electrolytes are shown in the manuscript in Table S1. Raman spectra were corrected for Rayleigh scattering.

Raman spectra of bromine Br₂

![Raman spectra of bromine Br₂](image2)

Figure S2: Raman spectrum of bromine Br₂, shown for a Raman shifts between \( \tilde{\nu} = 100 \) and 350 cm\(^{-1}\). Selected range for Raman shifts exclusively depicts Raman bands for polybromides and bromine. Raman spectrum was corrected for Rayleigh scattering. Red line shows the fitting of the spectra by the integration method according to Levenspiel-Marquart with the Lorentz method for symmetrical Raman stretching band of Br₂.
Raman spectra of HBr/Br₂/H₂O electrolytes including fitting of symmetrical and antisymmetrical Raman stretching bands of tri-, penta- and heptabromide.

Figure S3: Raman spectra of different HBr/Br₂/H₂O electrolytes depending on the state of charge SOC (SOC 0 % to SOC 35 %), shown for a Raman shifts between $\bar{v} = 100$ and 350 cm$^{-1}$. Selected range for Raman shifts exclusively depicts Raman bands for polybromides and bromine. Mixing conditions of the electrolytes are shown in the manuscript in Table S1. Raman spectra were corrected for Rayleigh scattering. Coloured lines show the fitting of the spectra by the integration method according to Levenspiel-Maquart with the Lorentz method for symmetrical and asymmetrical Raman stretching bands of the polybromides Br$_3$-, Br$_5$- and Br$_7$-.
Figure S4: Raman spectra of different HBr/Br2/H2O electrolytes depending on the state of charge SOC (SOC 40% to SOC 75%), shown for a Raman shifts between $\tilde{\nu} = 100$ and 350 cm$^{-1}$. Selected range for Raman shifts exclusively depicts Raman bands for polybromides and bromine. Mixing conditions of the electrolytes are shown in the manuscript in Table S1. Raman spectra were corrected for Rayleigh scattering. Coloured lines show the fitting of the spectra by the integration method according to Levenspiel-Marquart with the Lorentz method for symmetrical and asymmetrical Raman stretching bands of the polybromides Br$_3$, Br$_5$, and Br$_7$. 

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Figure S5: Raman spectra of different HBr/Br₂/H₂O electrolytes depending on the state of charge SOC (SOC 80 % to SOC 115 %), shown for a Raman shifts between \( \bar{\nu} = 100 \) and 350 cm\(^{-1}\). Selected range for Raman shifts exclusively depicts Raman bands for polybromides and bromine. Mixing conditions of the electrolytes are shown in the manuscript in Table S1. Raman spectra were corrected for Rayleigh scattering. Coloured lines show the fitting of the spectra by the integration method according to Levenspiel-Marquart with the Lorentz method for symmetrical and asymmetrical Raman stretching bands of the polybromides \( \text{Br}_3^- \), \( \text{Br}_5^- \) and \( \text{Br}_7^- \). For SOC \( \geq 100 \% \) at \( \bar{\nu} = 311 \text{ cm}^{-1} \) an overlapping becomes visible which can be assigned to elemental bromine. A second phase of bromine is already present here due to the solubility limit. Bromine is also present in small amounts in the aqueous solution.
Table S1: Assignment of concentrations of HBr and Br\(_2\) of the electrolyte to the respective SOC and the sample number.

| Sample no. | SOC | c(Br\(_2\)) | c(HBr) |
|------------|-----|-------------|--------|
|            | %   | mol L\(^{-1}\) | mol L\(^{-1}\) |
| 1          | 0   | 7.700       |        |
| 2          | 5   | 7.365       |        |
| 3          | 10  | 7.030       |        |
| 4          | 15  | 6.695       |        |
| 5          | 20  | 6.360       |        |
| 6          | 25  | 6.025       |        |
| 7          | 30  | 5.690       |        |
| 8          | 33  | 5.489       |        |
| 9          | 40  | 5.020       |        |
| 10         | 45  | 4.685       |        |
| 11         | 50  | 4.350       |        |
| 12         | 55  | 4.015       |        |
| 13         | 60  | 3.680       |        |
| 14         | 66  | 3.278       |        |
| 15         | 70  | 3.010       |        |
| 16         | 75  | 2.675       |        |
| 17         | 80  | 2.340       |        |
| 18         | 85  | 2.005       |        |
| 19         | 90  | 1.670       |        |
| 20         | 95  | 1.335       |        |
| 21         | 100 | 1.000       |        |
| 22         | 105 | 0.665       |        |
| 23         | 110 | 0.330       |        |
| 24         | 115 | 0.000       |        |

Table S2: Distribution of bromine to the polybromides x(Br\(_3\)), x(Br\(_5\)) and x(Br\(_7\)) and concentrations of the polybromides c(Br\(_3\)), c(Br\(_5\)) and c(Br\(_7\)) in aqueous electrolyte solution.

| Sample no. | SOC | x(Br\(_3\)) | x(Br\(_5\)) | x(Br\(_7\)) | c(Br\(_3\)) / M | c(Br\(_5\)) / M | c(Br\(_7\)) / M |
|------------|-----|-------------|-------------|-------------|-----------------|-----------------|-----------------|
| 1          | 0   | -           | -           | -           | -               | -               | -               |
| 2          | 5   | 0.343       | 0.623       | 0.034       | 0.057           | 0.052           | 0.002           |
| 3          | 10  | 0.296       | 0.691       | 0.014       | 0.099           | 0.116           | 0.002           |
| 4          | 15  | 0.289       | 0.698       | 0.013       | 0.145           | 0.175           | 0.002           |
| 5          | 20  | 0.290       | 0.699       | 0.011       | 0.194           | 0.234           | 0.003           |
| 6          | 25  | 0.295       | 0.683       | 0.023       | 0.247           | 0.286           | 0.006           |
| 7          | 30  | 0.290       | 0.687       | 0.023       | 0.291           | 0.345           | 0.008           |
| 8          | 33  | 0.300       | 0.666       | 0.034       | 0.331           | 0.386           | 0.013           |
| 9          | 40  | 0.299       | 0.683       | 0.018       | 0.401           | 0.457           | 0.008           |
| 10         | 45  | 0.301       | 0.680       | 0.019       | 0.453           | 0.513           | 0.010           |
| 11         | 50  | 0.296       | 0.679       | 0.025       | 0.496           | 0.569           | 0.014           |
| 12         | 55  | 0.288       | 0.681       | 0.030       | 0.531           | 0.628           | 0.019           |
| 13         | 60  | 0.283       | 0.679       | 0.039       | 0.568           | 0.682           | 0.026           |
| 14         | 65  | 0.265       | 0.676       | 0.059       | 0.585           | 0.747           | 0.044           |
| 15         | 70  | 0.247       | 0.664       | 0.089       | 0.580           | 0.778           | 0.069           |
| 16         | 75  | 0.221       | 0.637       | 0.143       | 0.554           | 0.800           | 0.120           |
| 17         | 80  | 0.187       | 0.592       | 0.220       | 0.502           | 0.794           | 0.197           |
| 18         | 85  | 0.146       | 0.518       | 0.337       | 0.414           | 0.737           | 0.320           |
| 19         | 90  | 0.117       | 0.384       | 0.499       | 0.340           | 0.555           | 0.481           |
| 20         | 95  | 0.123       | 0.409       | 0.468       | 0.273           | 0.455           | 0.347           |
| 21         | 100 | 0.151       | 0.381       | 0.467       | 0.249           | 0.314           | 0.256           |
| 22         | 105 | 0.157       | 0.361       | 0.482       | 0.173           | 0.200           | 0.178           |
| 23         | 110 | 0.187       | 0.307       | 0.506       | 0.115           | 0.094           | 0.103           |
| 24         | 115 | -           | -           | -           | -               | -               | -               |
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