Currently one of the biggest challenges of further expansion of renewable PV and wind electricity is cost efficient storage. Here redox flow batteries (RFB) are generally considered to have low-cost potential, because of independent scaling of power and capacity, long cycle life, and flexibility in configuration and operation. Among the different RFB chemistries, all-vanadium RFBs are closest to a large commercial breakthrough due to its high reversibility, long life cycle, and minor cross-over issues. Nonetheless, further commercialization of vanadium RFBs is challenged by increasing cost of vanadium pentaoxide that has more than doubled during the past years, and nowadays it accounts for >40% of the total capital costs of vanadium RFBs. For this reason there is a need for investigations and development of more cost-effective (organic) redox species that decreases the capital costs of RFBs.

Various types of all-organic and semi-organic RFBs have been proposed during the past couple of years. Many of them suffer from low cell potential and low peak galvanic power density compared to the state-of-the-art vanadium redox flow battery. In general the cell power density scales with the cell potential squared and is inversely proportional to the internal cell resistance. The cell resistance is a sum of the contributions from electrical and membrane resistances, charge transfer resistance and mass transfer limitations, and the best performance in general is achieved with cation exchange membranes, protons as charge carriers and carbon papers as electrodes with high specific surface area. High current densities can be achieved even when electrochemical reaction kinetics are slow and charge transfer resistance is high by using porous carbon papers with a large specific surface.

One method to increase the cell potential in all-organic and semi-organic RFBs is by pH tuning of the whole cell or by differential pH in the two half cells. This method is applicable because the redox potential of organic redox pairs typically displays a strong pH dependence because the redox reactions involve protons, which typically is not the case for metals. The concept of differential pH batteries has earlier been applied. Additionally, we recently demonstrated a semi-organic differential pH quinone-bromide battery based on bromide operated at pH~2 on the positive side and anthraquinone-2,7-disulfonate (AQDS) disodium operated at pH~8 on the negative side that was successfully operated over a period of 30 days. A cell potential as high as 1.3 V was achieved in that work, nonetheless, we obtained power densities that were significantly lower than the ones in the analogous acidic quinone-bromide battery. Despite similar reaction rate constants for the redox reactions, it was speculated whether the poorer performance was related to a non-optimized cell design, or higher electrolyte resistance because the AQDS side was operated close to neutral pH. To answer these questions we have in the present made a comparative study between an acidic and a differential pH quinone-bromide battery under semi-optimized conditions where the internal battery resistance is minimized with respect to redox solution composition, flow rate, electrode and membrane thickness. The comparison between the two battery chemistries are done in terms of battery polarization curves and electrochemical impedance spectroscopy (EIS). Additionally, the performance of the differential pH and acidic batteries were compared to standard vanadium RFB in the same cell.

Redox solutions.—Three different flow battery chemistries were investigated: differential pH quinone-bromide, acidic quinone-bromide and all-vanadium. Table I shows the compositions of the redox solutions used in the different batteries. Na2AQDS (9,10-anthraquinone-2,7-disulfonic acid disodium salt, 95% pure) was purchased from Combi-Blocks. Br2 (bromine, 99.99% pure) and NH4Br (ammonium bromide, ≥99.0% pure) were obtained from Sigma-Aldrich. H2AQDS (9,10-anthraquinone-2,7-disulfonic acid) the sodium-free form of Na2AQDS was produced by flushing Na2AQDS twice through a column containing Amberlyst 15H ion-exchange resin. H2SO4 (sulfuric acid, 95–98%) and HBr (hydrobromic acid, ≥48%) were purchased from Sigma-Aldrich. The mixture of V2+ (V2(SO4)3) and V4+ (VOSO4) in 2 M H2SO4 was provided by GfE company (Gesellschaft für Elektrometallurgie mbH).

Pretreatment of electrodes and membrane.—For all battery tests, carbon papers (SIGRACET, Type GDL 34 AA) and Nafion 212 and Nafion 117 cation exchange membranes were used. Carbon papers were treated by oxidation at 500°C in air for 7 hours to increase their hydrophilicity. Untreated Nafion 212 was used in the differential pH quinone-bromide RFB. However, in the case of acidic quinone-bromide and vanadium RFB, Nafion 212 was treated by 30 min boiling in H2O2 (3 wt%), then 10 min rinsing with deionized water. Afterward, the membrane was transferred to 0.5 M H2SO4 at 90°C followed by rinsing several times in warm deionized water.

Electrochemical impedance spectroscopy & cell optimization.— Electrochemical impedance spectroscopy (EIS) was performed to quantify the electrical (Ri) and charge-transfer contributions (Rct) to the total cell resistance (Rtot = Rei + Rct) in order to investigate the effect of the thickness of the electrode and membrane, circulation
flow rate of redox solutions, and concentration of redox species. The number of carbon papers was varied from 3 to 10 on each side of the cell; the performance of two proton exchange membranes with similar ion-exchange capacity but different thicknesses (Nafion 117 and 212) was compared; the flow rate of positive and negative electrolytes was adjusted to 20, 50, 80 and 120 ml/min; and lastly, the effect of concentration of Na2AQDS and on cell resistance was studied. Electrochemical impedance spectroscopy (EIS) and polarization curve measurements were used to examine the influence of the studied parameters on the cell resistance. EIS was performed with a CH Instruments 660E potentiostat under different experimental conditions in a frequency range between 0.01 Hz and 10 MHz with a perturbation amplitude of 5 mV. For comparison to EIS data, polarization curves were measured by charging and discharging the battery at constant current density. All polarization curves data were collected using battery testing system (Neware BTS-5V3A). During the test, data points in the polarization curve were recorded symmetrically by first setting a discharge current at fixed value and the record the cell voltage for 60 s, followed by a short resting period, and then charging with the same current for 60 s. Subsequent data points at other currents were recorded similarly. The potential in the polarization curve was the average over the 60 s interval, but did not change more than a few percent. The symmetric test procedure ensured that the state-of-charge (SOC) did not change significantly during the recording of the whole polarization curve at a specific (SOC). Only data for the discharge test are shown in the polarization curves.

**Battery tests in optimal configuration.**—Charge/discharge tests were performed in the cell depicted in Fig. S1. It consists of two Poco graphite plates with serpentine flow field provided from Fuel Cell Technologies (FCT). Thermally treated carbon papers with nominal thickness of 230 μm and geometric area of 4 cm² were used as electrodes. Five layers of carbon papers were used in each half-cell separated by a Nafion 212 membrane (thickness 50 μm in dry conditions). The cell was sealed with two Viton gaskets with the thickness of 0.5 mm and 1 mm when using three and five electrodes on each side of the cell, respectively. In the case of 10 electrodes on each side of the cell two Viton gaskets with thickness of 1 mm were used. The flow cell was assembled using two 8 mm × 12 cm × 12 cm steel endplates and seven bolts tightened with a torque of 4.5 N m. The redox solutions volumes were 5 ml and 25 ml on the negative and positive side, respectively. During all RFB tests, the negative side was under the nitrogen atmosphere. All battery tests were performed at room temperature except for the measurements of the differential pressure battery which was measured at both room temperature and 40°C. A two-channel Intelligent BT600L peristaltic pump was used to circulate the redox solutions at 120 ml/min. Charge/discharge measurements were carried out by using battery testing system (Neware BTS-5V3A) in a four-wire configuration. The differential pH quinone-bromide cell was charged at different current densities using upper cutoff voltage of 1.5 V and lower cutoff voltage of 0.4 V.

**Results and Discussion**

**Cell optimization.**—**Thickness of the carbon electrode.**—EIS measurements were performed with 3, 5 and 10 carbon papers on each side of the cell with different current density of 27%, 13% and 13%, respectively. The flow rate and concentration of redox species were kept at maximum (120 ml/min and 0.5 M Na2AQDS and 0.3 M Br2 in 2 M NH4Br) with a Nafion 212 cation exchange membrane as separator. Fig. 1a shows the Nyquist plots for different number of the carbon paper electrodes. All data reported in the Nyquist plots (Figs. 1a to 1d) have been described with the equivalent circuit presented in Fig. 1e (see Eq. (S1) in Supplementary Information, section S2) using MEISIP software and the results of the fits are presented in section 2 of Supplementary Information. In the Nyquist plots we interpret the first intercept (typically 10⁵–10⁶ Hz) with the real axis (Z'' = 0) as the pure ohmic electrical and ion resistance (Rct = R + Rct). This consists of contributions from electro transport in the cell (Rct), i.e. current collectors, graphite blocks, carbon paper electrodes and contact resistances between the carbon paper electrodes.24,25 Here it is safe to assume that only the contact resistances have significant contributions. The ion resistance (Rct) has combined contributions from the membrane and electrolyte. Finally, we interpret the second and third intercept (Hz range) with the real axis as charge-transfer resistance (Rct = Rct + Rct) from the anode (Rct) and cathode (Rct) sides. Attribution of second and third resistance to anode and cathode, respectively, is based on the electrochemical reaction rate of Na2AQDS and Br2/ Br⁻ redox couples. Based on standard heterogeneous electron transfer rate constant (k') of Na2AQDS at pH = 8.19 and Br2/Br⁻ redox couple,3,26 the charge transfer resistance of Br2/Br⁻ is ~12 times greater than Na2AQDS. Supplementary Information, section S3) However, we did not observe this ratio in our experiments (Supplementary Information, section S2) where the Rct/Rct ratios are of the order 1–2 depending on the experimental conditions. This indicates that effective thicknesses of the electrodes that are involved in the electrochemical reactions are larger for the Br2/Br⁻ side. Furthermore, it also indicates that only a small fraction of the electrodes close to the membrane surface are involved in the electrochemical reactions. As can be seen from Fig. 1a and Table II, the number of carbon paper electrodes affects both Rct and Rct. Rct only varies between 0.59 Ω cm² and 0.68 Ω cm² for 5 and 10 carbon papers, respectively. A constant Rct is expected if it is dominated by the membrane resistance. Nonetheless, we attribute the small variation in Rct mainly to the contact resistance of electrodes and compression of membrane. By decreasing the number of the electrodes from 10 to 5, the porosity/compression remains constant but the contact resistance is decreased as seen by the relatively small decrease of Rct.27-33 Further reduction to 3 carbon papers, increases Rct slightly which is somewhat counterintuitive. However the increase was very small (0.03 Ω cm²) and we anticipate that the higher compression leads to a lower solution uptake in the membrane and hence a lower ion conductivity.34-36 Moving the attention to Rct, it is seen that Rct decreases slightly with the number of carbon that Rct increases from 0.43 Ω cm² to 0.63 Ω cm² for 5 and 10 papers, respectively, while it is in between with 0.58 Ω cm² for 3 papers. The interpretation of these results is not straightforward. On one hand it is expected that increasing the number of carbon papers will lead to higher surface area and thus reduce Rct.30-33 However, this does not account for the changes in the fluid dynamic; indeed the local velocity close to the membrane-electrode interface will decrease as the number of carbon papers is increased because of the higher hydraulic resistance. For this reason, it is anticipated that the minimum Rct observed for 5 carbon papers is a trade-off between high electrode surface area and optimized electrolyte circulation through carbon papers. Based on these results five carbon papers are found the optimal value of the number of electrodes among the experimental conditions tested in the present work. Furthermore, battery polarization curves at different thicknesses of electrodes (Fig. S4) provide independent measurements of Rct which are in excellent agreement with the EIS measurements as seen in Table II.

### Table I. Compositions used in the three different battery chemistries.

<table>
<thead>
<tr>
<th>Battery</th>
<th>Negative side</th>
<th>Positive side</th>
</tr>
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<tbody>
<tr>
<td>Differential Ph quinone-bromide</td>
<td>0.5 M Na2AQDS in 2 M NH4Br</td>
<td>0.3 M Br2 in 2 M NH4Br</td>
</tr>
<tr>
<td>Acidic quinone-Bromide</td>
<td>1 M H2AQDS in 1 M H2SO4</td>
<td>0.5 M Br2 in 3 M HBr</td>
</tr>
<tr>
<td>Vanadium</td>
<td>1.6 M mixture of V⁵⁺ and V⁶⁺ in 2 M H2SO4</td>
<td>1.6 M mixture of V³⁺ and V⁴⁺ in 2 M H2SO4</td>
</tr>
</tbody>
</table>
Membrane thickness effect on cell resistance.—$R_{ei}$ includes a relatively large contribution from the membrane (Supplementary Information, section S5) and is expected to be approximately linear with its thickness. In the present work, we compared the cell performance using untreated Nafion 117 (183 $\mu$m) and untreated Nafion 212 (53 $\mu$m). In both cases, five carbon papers were used on each side of the cell and other operational conditions were kept as in the previous set of experiments with a flow rate of 120 ml/min, 0.5 M Na$_2$AQDS and 0.3 M Br$_2$ in 2 M NH$_4$Br. As can be seen in Fig. 1b and Table S2b, both $R_{ei}$ and $R_{tot}$ are significantly decreased by switching Nafion 117 to Nafion 212. These results are in agreement with polarization curve results (Fig. S6) and with previous similar study on vanadium redox flow battery. It is worth to notice that these two membranes have very similar characteristics i.e. ion exchange capacity (0.9 and 0.91 meq/g) and solution uptake ($\sim$20 and 21 H$_2$O per SO$_3^-$) of Nafion 117 and 212, respectively, even though our experiments showed a different out-of-plane swelling. The morphological differences are expected to have only minor impact on the membrane resistivity and the resistance should scale with wet membrane thickness ratio which is about 3.5. The relative change of $R_{ei}$ is only about 2.2 and the difference can be attributed to electrical resistance in the cell (carbon paper, contact resistance, etc) and solution ionic resistance.

Figure 1. EIS analysis for optimization of the flow cell: (a) Influence of different number of carbon papers on cell resistance (Experimental conditions: flow rate of 120 ml/min, 0.5 M Na$_2$AQDS and 0.3 M Br$_2$ in 2 M NH$_4$Br, and Nafion 212); (b) Comparison of ionic resistance of Nafion 117 and Nafion 212 (Experimental conditions: 5 carbon papers on each side of the cell, flow rate of 120 ml/min, 0.5 M Na$_2$AQDS and 0.3 M Br$_2$ in 2 M NH$_4$Br); (c) Influence of different flow rates on cell resistance (Experimental conditions: 5 carbon papers on each side of the cell, Nafion 212, 0.5 M Na$_2$AQDS and 0.3 M Br$_2$ in 2 M NH$_4$Br); (d) Low concentration (0.05 M Na$_2$AQDS (negative side) and 0.1 M Br$_2$ (positive side) in 2M NH$_4$Br) against High concentrations (0.5 M Na$_2$AQDS (negative side) and 0.3 M Br$_2$ (positive side) in 2M NH$_4$Br) (Experimental conditions: 5 carbon papers on each side of the cell, flow rate of 120 ml/min, Nafion 212). Insets show the magnification of each graph in the region associated to the ohmic resistance. All measurements were done at 50% state of charge (SOC). (e) Equivalent electrical circuit used in the analysis of the four-point Electrochemical Impedance Spectroscopy.
Table II. EIS analysis for the influence of number of electrodes on cell resistance.

<table>
<thead>
<tr>
<th>Number of carbon papers</th>
<th>Equivalent compression</th>
<th>3</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_\text{e}$ ($\Omega \text{cm}^2$)</td>
<td>0.23</td>
<td>0.23</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>$R_\text{ct}$ ($\Omega \text{cm}^2$)</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>$R_{\text{ref}}$ from polarization curves ($\Omega \text{cm}^2$)</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td></td>
</tr>
</tbody>
</table>

Differential pH quinone-bromide battery performance.—The battery tests were run for the optimal conditions presented in Table III to evaluate the performance of optimized RFB. The theoretical capacity of the differential pH battery using 0.5 M of Na$_2$AQDS and based on 1.5 electrons accessible per Na$_2$AQDS molecule is 101 mAh. The discharge capacity value at different current densities (Fig. 2a), varies from 99 mAh at 30 mA/cm$^2$ to 65.3 mAh at 250 mA/cm$^2$. The decreasing capacity with higher current densities is due to the higher overvoltage because of the non-zero internal cell resistance. This is also reflected in voltage efficiency which decreases from about 95% to less than 65% when current density is increased from 30 to 250 mA/cm$^2$ (Fig. S8). Given that energy efficiency is directly proportional to the voltage efficiency this also explains its 38% reduction at higher current densities (Fig. 2b). The current efficiency increases from 97.0% to 99.6% when the current density is increased from 30 mA/cm$^2$ to 250 mA/cm$^2$ (Fig. 2b). This is a consequence of shorter charging/discharging times at high currents and thus lower self-discharge, which mainly is caused by bromine crossover in the membrane. The charge/dischARGE curves shown in the Fig. 2c have a Nernstian behavior as reported previously. With respect to the stability, the differential pH battery was operated for 100 charge/discharge cycles (Fig. 2d), and in our previous study for 30 days. We partly ascribe the pH stability of negative electrolyte at pH~8 and disequilibrium of negative and positive electrolytes after 100 cycles to the: i) presence of buffers NH$_3$/NH$_4$ and H$_2$CO$_3$/HCO$_3^-$ determined by the supporting electrolyte (NH$_4$Br) and CO$_3^{2-}$ bound in Na$_2$AQDS, respectively and ii) a less well-understood net/asyymmetric transport of protons to the bromide side during battery cycling that balances the transport of Br$_2$ and HBr to the Na$_2$AQDS side. This is discussed in detail in Ref. 19.

Nonetheless, during one charge/discharge cycle, the pH of Na$_2$AQDS side varies significantly (see e.g. Fig. S9a in Ref. 19) mainly due to the involvement of protons in reduction/oxidation of Na$_2$AQDS. During battery cycling in the present study we did not observe any sudden drops in the cell potential during 100 cycles (‘shoulders’ in Fig. S9a in Ref. 19) due to pH values below 5 on the Na$_2$AQDS side. This was mainly because the Na$_2$AQDS side was well-sealed under N$_2$ atmosphere, whereby CO$_2$ could not escape the system, contrary to the tests in Fig. S9a in Ref. 19 where the Na$_2$AQDS side was opened regularly for pH measurements and CO$_2$ could escape.

The average stable current efficiency of 99.5% was achieved after 100 cycles, which is a major improvement with respect to 95% found in our previous work. Additionally, a capacity loss of 0.026% per cycle was observed during cycling which is ~50% less than previous non-optimized cell. Lower capacity loss is most likely a consequence of shorter cycling times due to higher current densities. Two possible capacity loss mechanisms can be identified: Na$_2$AQDS crossover through the membrane (from negative side to the positive side of the battery) and chemical degradation of Na$_2$AQDS during cycling. A wide scan cyclic voltammogram recorded for the electrolyte on the positive side of battery after 100 cycles (Fig. S9) shows that there is no evidence of the presence of Na$_2$AQDS on the positive, indicating that the capacity loss is related to chemical instability of Na$_2$AQDS.

Power density of the differential pH quinone-bromide battery.—The power density of differential pH quinone-bromide battery was obtained by running battery tests under the optimal conditions presented in Table III. Figs. 3a and 3b shows the polarization and power density curves at room temperature for differential pH quinone-bromide battery. The area resistance of around 1 $\Omega \text{cm}^2$ was achieved under optimal conditions which is 3.5 times lower than previous work. The peak galvanic power density of 0.4 W/cm$^2$ is found at 90% SOC and approximately 500 mA/cm$^2$ which is significantly higher than the previous work (Fig. S10). The power density of the differential pH battery can be boosted further up to 0.45 W/cm$^2$ by increasing the temperature to 40°C as shown in Figs. 3c and 3d.
Figure 2. (a) Discharge capacity vs. cycle number at different current densities; (b) Average current and voltage efficiencies vs. current density; (c) Charge/discharge cycles 1 to 5 at 150 mA/cm²; (d) Charge/discharge capacity measurement and current efficiency versus cycle numbers for 100 cycles at 150 mA/cm². Experimental conditions: under optimal conditions shown in Table III.

Figure 3. Polarization curves and power density calculations: (a) and (b) differential pH quinone-bromide battery at room temperature; (c) and (d) differential pH quinone-bromide battery at 40 °C.
high conductivity of electrolytes (2 M sulfuric acid) and lower diffusion coefficient and electron transfer rate constant while higher peak galvanic power density than both quinone-bromide batteries.

Conclusions

High cell potential and power density are key parameters for redox flow batteries. Previously, it has been shown that differential pH quinone-bromide battery delivers high cell potential of 1.3 V and poor power density. In this work, we have studied effect of several factors to minimize the cell resistance and consequently improve the output power density. The cell resistance was reduced by using optimal conditions for the thickness of electrodes, flow rate, membrane thickness and concentration of redox species. The differential pH quinone-bromide battery under optimal conditions has an area resistance of 1 MΩ cm² and a maximum power density of 0.45 W/cm². The power density value is 12% higher than acidic quinone-bromide battery and somewhat more lower than the highest value for vanadium redox flow battery under the identical conditions. Given the results shown in this work it is realistic that with further cell optimization, e.g. flow field geometry, electrode compression, and membrane morphology, the differential pH quinone-bromide battery can reach performance similar to the acidic quinone-bromide and vanadium RFB.

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