

Porto novo flow batteries

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Analysis of the prior art¹⁹ demonstrates the development in 2011 of an all-alkaline PSA RFB system with alkaline-based oxygen(air) redox couple and a polysulfide redox couple, separated by an anion-exchange membrane (AEM). During the discharge process, shorter-chain-length polysulfides are oxidised into longer-chain-length polysulfides in the anolyte while O₂ is reduced to OH⁻ in the catholyte, and vice versa. The reactions of both half-cells and the overall cell reaction are summarised in Eqs. 1-3, based on which the alkaline PSA RFB has a standard equilibrium potential of 0.88 V.

Although this alkaline PSA RFB shows great promise for large-scale energy storage, there are several scientific challenges, such as the development of low-cost catalysts for the polysulfide and oxygen reactions, as well as the crossover of polysulfide through AEMs.

a RFB based on single anion-exchange membrane. b RFB based on single cation-exchange membrane. c RFB based on double-membrane design combining anion-exchange membrane and cation-exchange membrane.

In recent work on PSA RFBs, termed air-breathing aqueous sulfur flow batteries²⁴, Chiang and co-workers demonstrated the operation of the flow battery by using acidic-catholyte (Li₂SO₄ in H₂SO₄) and alkaline polysulfide anolyte (Li₂S₂ in LiOH) separated by a ceramic electrolyte (Lithium Super Ionic Conductor, or LiSICON). PGM catalysts were used for the OER/ORR reactions, such as platinum mesh or dual cathodes coated with IrO₂ as OER catalyst and Pt black as the ORR catalyst. However, the PGM catalysts and LiSICON membrane used in their demonstration work are expensive, and the high membrane resistance limits the power density. Low-cost membranes and non-PGM catalysts are still required to further improve the scalability of the PSA flow battery system.

a Diagram of sulfidized Ni foam electrode and MnO₂-based air electrode for OER and ORR reactions. b, c SEM images of the commercial MnO₂-based air electrode. d Photo of the as-received Ni foam. e, f SEM images of the as-received Ni foam. g Photo of the sulfidised Ni foam. h, i SEM images of the sulfidised Ni foam. j, k XPS core level spectra of the sulfidised Ni foam. l Polarisation measurements of the as-received and sulfidised Ni foams.

The overall performance enhancement of sulfidised nickel can be explained by the enhanced electron transfer

from the strongly coupled Ni/NiS_x interface^{30,31} and the much faster polysulfide adsorption/desorption rate from the transient metal sulphide surface compared with the partly sulfidised metal surface³². The more significant improvement on the cathodic branch is consistent with previous observations³³. This indicates NiS_x plays a vital role in the electrochemical reduction of polysulfide species. However, detailed analysis of this phenomena merits in-depth study in the future.

a Left: H-cell setup for polysulfide crossover determination on single-AEM (FAA-3-PK-130) and CEM (Nafion 117); Right: redox flow battery setup for polysulfide crossover determination on the dual-membrane structure. b Cumulative crossover of the permeate solution in single-AEM, single-CEM and dual-membrane setup against permeation time, inset shows the dual-membrane polysulfide crossover measured at the air side. c Calculated polysulfide flux across single-AEM, single-CEM and dual-membrane structure. d EIS of CEM and AEM. e The polysulfide flux versus membrane conductivity. The error bars show the UV-Vis measurement error, conductivity measurement error and fitting errors.

The ohmic resistance of FAA-3-PK-130 AEM and Nafion 117 CEM in 1 M NaOH solution was determined as the intercept of the impedance signal with the Z_{real} axis in the complex impedance plot (Fig. 3d) obtained via electrochemical impedance spectroscopy (EIS) measurements. The AEM shows 1/3 the ohmic resistance of the CEM (0.46 ± 0.01 vs. 1.44 ± 0.03 Ω cm²), showing that the AEM enables a faster rate of ion transport. The relation of sulfur crossover rate versus conductivity of AEM and CEM are shown in Fig. 3e. The AEM exhibits 3.1 times conductivity and 32.9 times polysulfide crossover flux compared with the CEM.

a Experimental setup of single-membrane-structured PSA RFB. b Experimental setup of dual-membrane-structured PSA RFB. c Voltage profile of the PSA RFB with FAA-3-PK-130 AEM over 10 cycles. d Voltage profile of the PSA RFB with Nafion 117 CEM over 20 cycles. e Voltage profile of the PSA RFB with both FAA-3-PK-130 AEM and Nafion 117 CEM over 80 cycles. f Voltage efficiencies against cycle number of the PSA RFBs with either single or dual membranes. g Coulombic efficiencies against cycle number of the PSA RFBs with either single or dual membranes. (inset figure shows the minified scale for showing the Coulombic efficiency degradation of single-AEM cell). h Round-trip energy efficiencies against cycle number of the PSA RFBs with either single or dual membranes.

a Polarisation curve and power density curve at 25 °C and various SOc. b Polarisation curve and power density curve at 50% SOC and various temperatures. c Measured half-cell overpotentials against current density at 25 °C and 50% SOc. d measured polysulfide-side half-cell potential profile against capacity. e Measured air-side half-cell potential profile against capacity. f Round-trip energy efficiency against current density.

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