A high power thermally regenerative ammonia-copper redox flow battery enabled by a zero gap cell design, low-resistant membranes and electrode coatings

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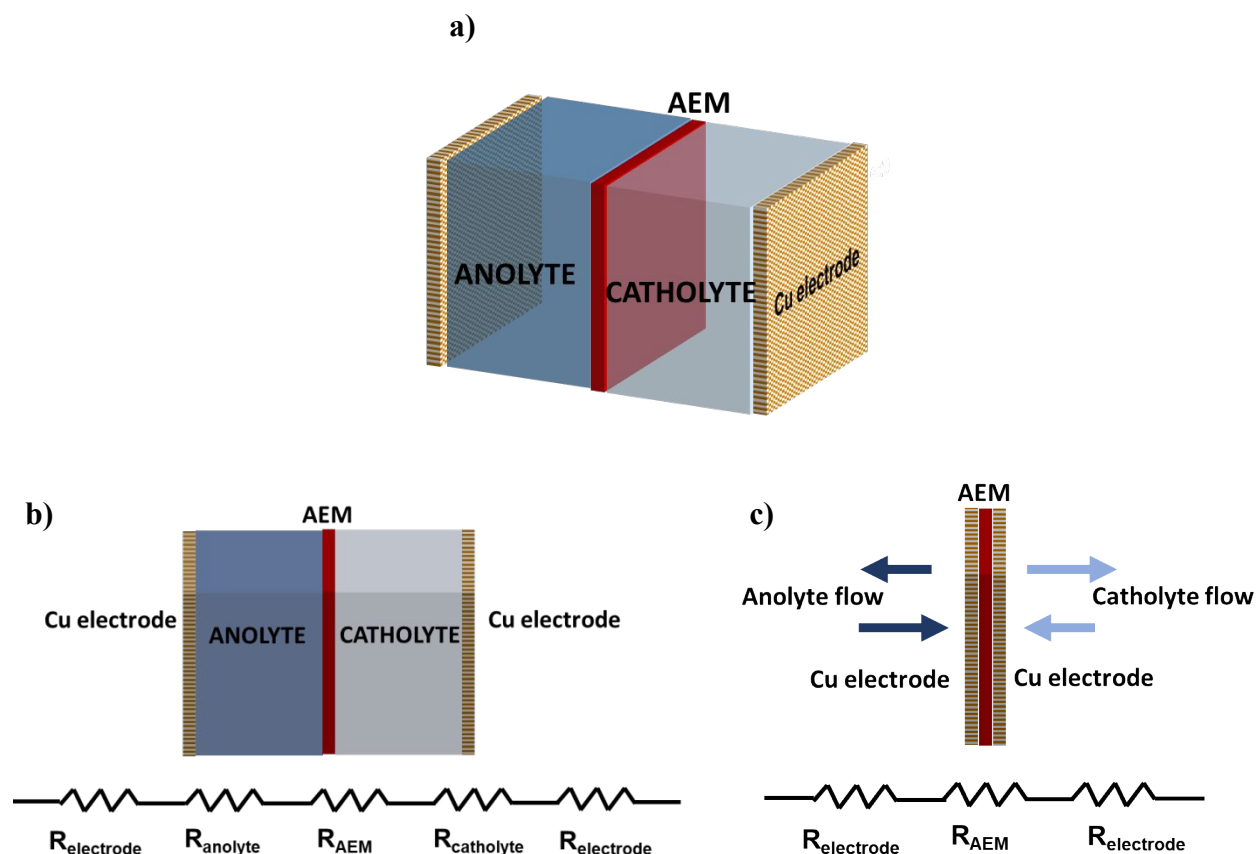*Corresponding authors: carges@lsu.edu; xzhu@lsu.edu

Figure S1. a) Schematic figure of a non-zero gap TRAB (i.e., a closed batch system); **b)** Sources of resistances within a non-zero gap closed batch setup; **c)** Sources of resistances in a zero gap flow mode operation.

Preparation of QASEBS AEMs

Chloromethylation of SEBS was carried out using the procedure by Wang *et al.*[1] SEBS was dissolved in chlorobenzene at room temperature to prepare a 2 wt% solution in a round bottom flask with equipped with a magnetic stir bar. Paraformaldehyde and chlorotrimethylsilane (5:5:1 molar ratio to SEBS repeat unit) was added to the flask. The flask was sealed with a rubber septum and the silicon oil bath containing the flask was heated to 80 °C. Then, $SnCl_4$ (Lewis acid catalyst), a 2 wt% ratio to SEBS added, was added slowly by syringe through the rubber septum. To monitor the degree of chloromethylation (DC) of SEBS, samples were extracted from the flask during the reaction. After withdrawing an aliquot from the flask, the chloromethylated SEBS (CMSEBS) solution was precipitated in methanol (5:1 volume ratio) and then vacuum filtered. The collected solid was analyzed via ^{1}H NMR with $CDCl_3$ as the solvent. The reaction was terminated once the degree of chloromethylation (DC) of SEBS was 0.13 (**Figure S2**; note: it took 7 days to complete the reaction). At the end of the reaction, the solution was cooled and precipitated in methanol using the aforementioned ratio. The solid was vacuum filtered, dried, re-dissolved in chloroform at 5 wt% and then precipitated in methanol (5:1 ratio) to remove impurities. The solid was collected by vacuum filtration and then vacuum dried for 16 hours at room temperature.

To prepare the QASEBS membrane, CMSEB was dissolved in chlorobenzene to prepare a 5 wt% solution. 9 mL of the CMSEBS solution was drop casted on to 9 cm x 9 cm glass plates and the solvent was evaporated from the membrane at 60 °C. The membrane was peeled off the glass plate and then immersed in a 40 wt% trimethylamine aqueous solution for 48 hours at room temperature. Afterwards, the membrane was rinsed with copious amounts of deionized water (DI H_2O) to remove residual trimethylamine and then dried in a fume hood overnight.
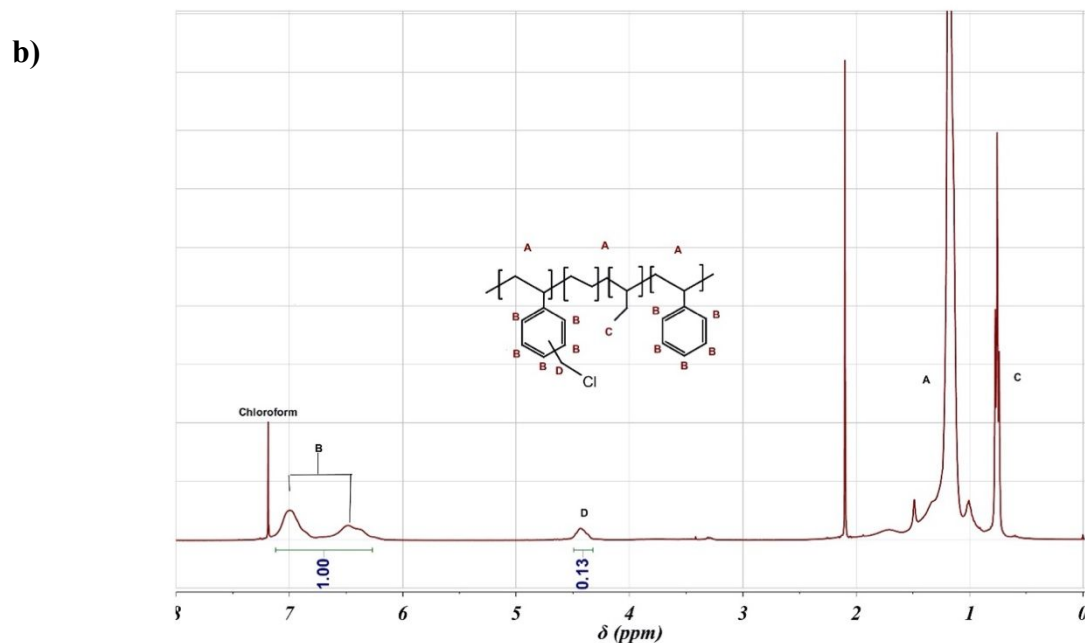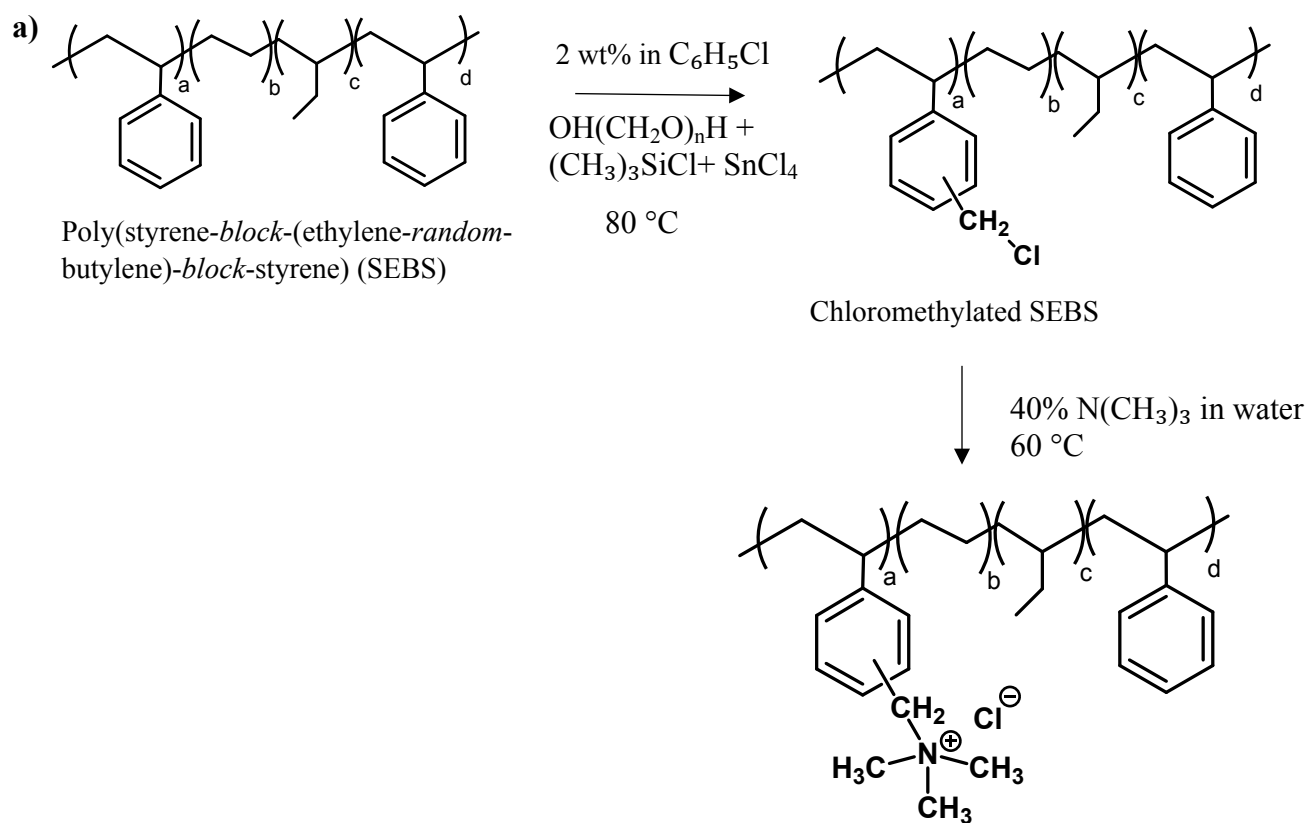
Figure S2. a) Reaction mechanism for preparing QASEBS. **b)** ^{1}H NMR spectrum for chloromethylated SEBS – a precursor for making QASEBS.

Degree of chloromethylation (DC) was calculated using Equation S1:

$$DC = \frac{\frac{Area(D)}{2}}{\frac{Area(B) + \frac{Area(D)}{2}}{5}} \times 0.34 \qquad \text{<S1>}$$

The degree of chloromethylation of CMSEBS obtained was 0.10 to 0.13.

Determining IEC of QASEBS in chloride anion form using Equation S2:

$$IEC\ [\mathrm{mmol\ g^{-1}}] = \frac{DC \cdot 1000}{(MW_{styrene} + DC \cdot (MW_{cation} + MW_{Cl} + MW_{-CH_2-} - 1))} \times 0.34 \qquad \text{<S2>}$$

$MW_{styrene}$: Molecular weight of styrene repeat unit (g mol^{-1})
MW_{cation} : Molecular weight of the substituted cationic site (g mol^{-1})

MW_{Cl} : Molecular weight of chloride ion

MW_{CH2}: Molecular weight of the methyl bridge connecting cation to the PS backbone (g mol^{-1})

The IEC calculated for QASEBS was 0.34 ± 0.03 mmol g^{-1}.

Note: <S2> is multiplied by 0.34 because poly(styrene) only makes up 34% (molar fraction) of SEBS.

Preparation of SPEEK ionomer coated copper mesh electrodes

SPEEK was prepared by first dissolving PEEK in concentrated sulfuric acid (10 wt% PEEK in 98 % pure sulfuric acid) and mixing the solution for 72 hours at 25 °C. The polymer was precipitated in an ice-cold bath and repeatedly washed and filtered until the pH of the washing water was 7. **Figure S3** provides the ^{1}H NMR of the prepared SPEEK batch. A 2 wt% SPEEK solution in n-methyl pyrrolidine (NMP) was prepared and the resulting solution was used as an ionomer solution. This solution was spray painted directly onto the Cu mesh. After several spray applications, the Cu mesh placed on a hotplate at 100 °C to evaporate the NMP solvent. The applications and drying was continued until a loading of 0.44-0.75 mg cm^{-2} SPEEK on a 5 cm^2 Cu mesh was achieved.
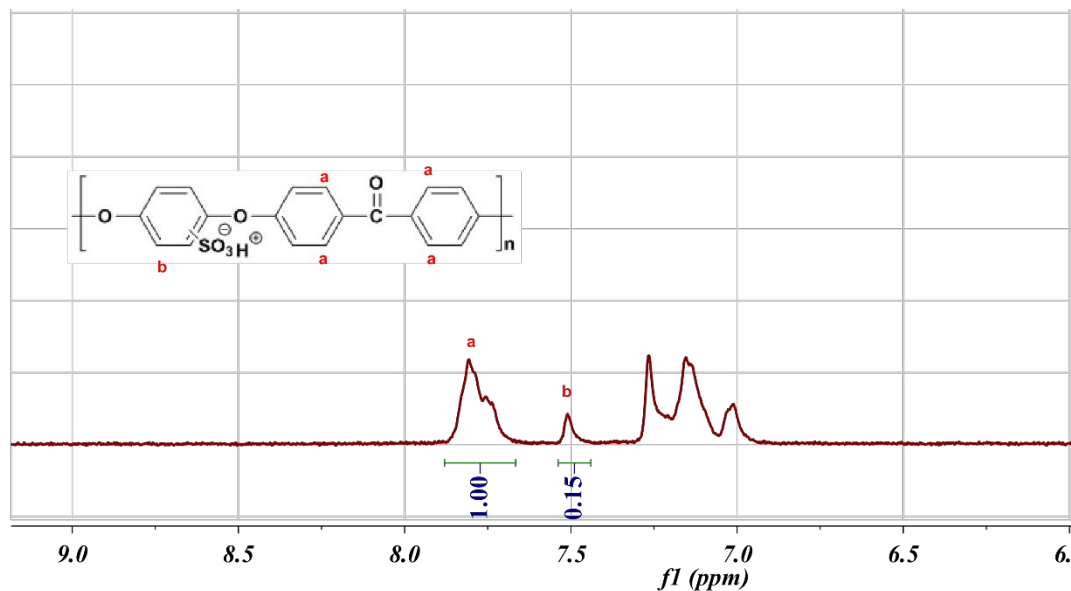
Figure S3. ^{1}H-NMR for SPEEK

The degree of sulfonation (DS) was determined using Equation S3:

$$DS = \frac{4 \cdot \text{Area}(\delta = 7.5)}{\text{Area}(\delta \approx 7.65 \text{ to } 8.1)} \tag{S3}$$

The DS of SPEEK was 0.56-0.60.

Determining IEC of SPEEK in the proton form was calculated using Equation S4:

$$\text{IEC} \left[\text{mmol g}^{-1}\right] = \frac{DS \cdot 1000}{\left(MW_{\text{PEEK,monomer}} + DS \cdot \left(MW_{SO3} + MW_{H^+} - 1\right)\right)} \tag{S4}$$

DS = Degree of sulfonation to PEEK (equation <2>)
$MW_{\text{PEEK, monomer}}$ = Molecular weight of PEEK repeat unit (g mol^{-1})
MW_{H^+} = Molecular weight of the sodium (g mol^{-1})

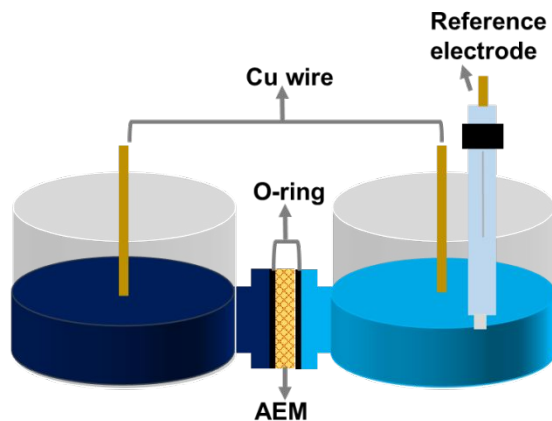The IEC of SPEEK was 1.61 ± 0.01 mmol g^{-1}.

Figure S4. Schematic of two-compartment glass cell (H-cell) used for non-zero gap mode operation and study of cathode side reaction kinetics.

The Tafel slope was extracted from the Tafel plot in **Fig. 7a** in the main manuscript. This Figure plotted log of current densities versus surface overpotential (η_s) obtained from the LSV data. To calculate η_s, the cell potential values (E) versus HgO/Hg/KOH were converted into E vs SHE, by adding the conversion factor for HgO/Hg/KOH to SHE (+0.098 V). The potential vs. SHE was iR corrected for each measured value at a particular current. The 'R' term in iR was determined from the HFR through impedance spectroscopy. This corrected potential value (E') was subtracted from the standard half-cell potential for the $Cu^{2+} + 2e^-$ → Cu reduction reaction in the cathode ($E^o_c = 0.34$ V). This yielded the surface overpotential (η_s) at different current density values. Equations S5- S7 were used for these calculations.

$$E_{iR\ corrected,c} = E_{measured,\ c}(vs\ SHE) - iR \qquad \text{<S5>}$$

$$\eta_{s,c} = E_{iR\ corrected,\ c} - E^0_c(vs\ SHE) \qquad \text{<S6>}$$

$$\log i = \frac{\alpha_c zF}{2.303RT}\eta_{s,c} + \log i_o \qquad \text{<S7>}$$

$E_{measured,\ c}(vs\ SHE)$: Cathode potential measured in Volts vs SHE

$E_{iR\ corrected,c}$: Cathode potential corrected for ohmic resistance from electrolyte in Volts

i: Current density in A cm^{-2}

i_o: Exchange- current density in A cm^{-2}

R: HFR measured using EIS in Ω cm^{-2}

E_c^0: Cathode equilibrium potential in Volts

$\eta_{s,c}$: Cathode surface overpotential in Volts

$\frac{\alpha_c zF}{2.303RT}$: Tafel slope term

Table S1. List of equivalent circuit model fit elements and their values for each configuration

Configuration	R_s (Ω)	R_{ct} (Ω)	W (Ω)	Y (F)	a
Non-coated Cu+QASEBS	0.24	2	0.27	0.00	0.8
SPEEK coated Cu+ QASEBS	0.19	0.69	0.45	0.00	0.8

REFERENCES

1. Z. Wang, J. Parrondo and V. Ramani. Polystyrene-Block-Poly(ethylene-ran-butylene)-Block-Polystyrene Triblock Copolymer Separators for a Vanadium-Cerium Redox Flow Battery. *J. Electrochem. Soc.*, 2017, **164**, F372–F378.