Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information (ESI)

All sprayed fluorine-free membrane electrode assembly for low-platinum and low-humidity proton exchange membrane fuel cells

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1. Fluorine-free proton-conducting ionomer preparation and characterization

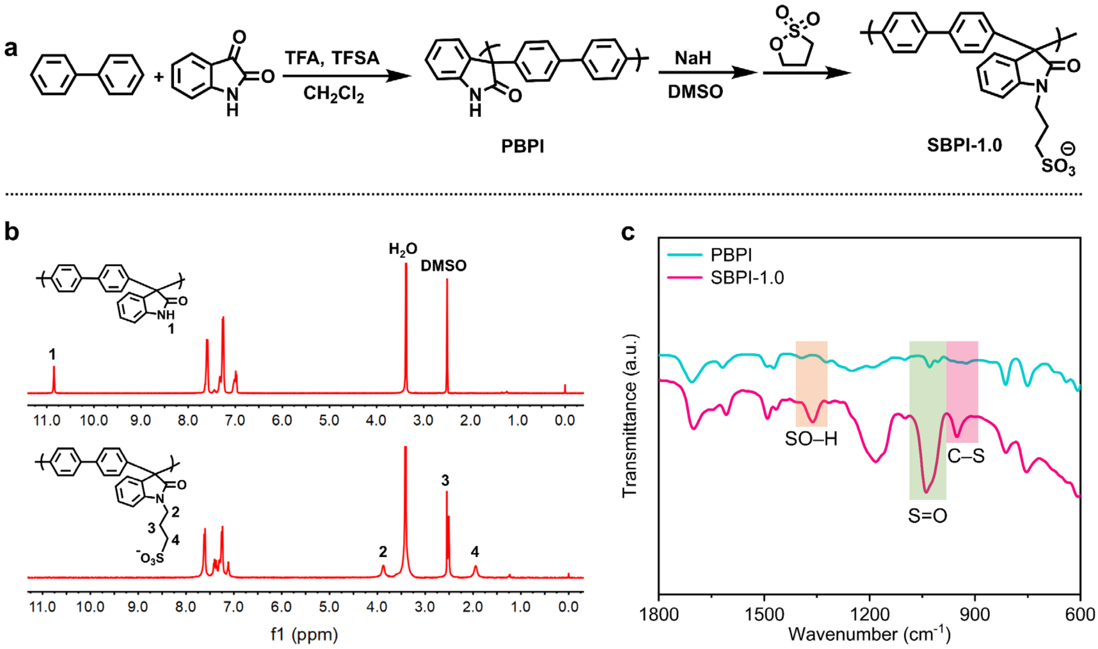

Fig. S1 Preparation and structural characterization of SBPI-1.0 ionomer. (a) Synthetic route of SBPI-1.0 ionomer. The fluorine-free ionomer was prepared by two-step reaction: 1) PBPI polymer precursor was prepared via a superacid-catalyzed polycondensations reaction from the two monomers; 2) SPBI-1.0 was prepared by grafting 1,3-propanesultone onto the reactive –NH group.[1] (b) ^{1}H NMR (400 MHz, 298 K, DMSO-d_6) spectra and (c) ATR-FTIR spectra of the PBPI polymer and SBPI-1.0 ionomer.

2. Fabrication of all sprayed MEA

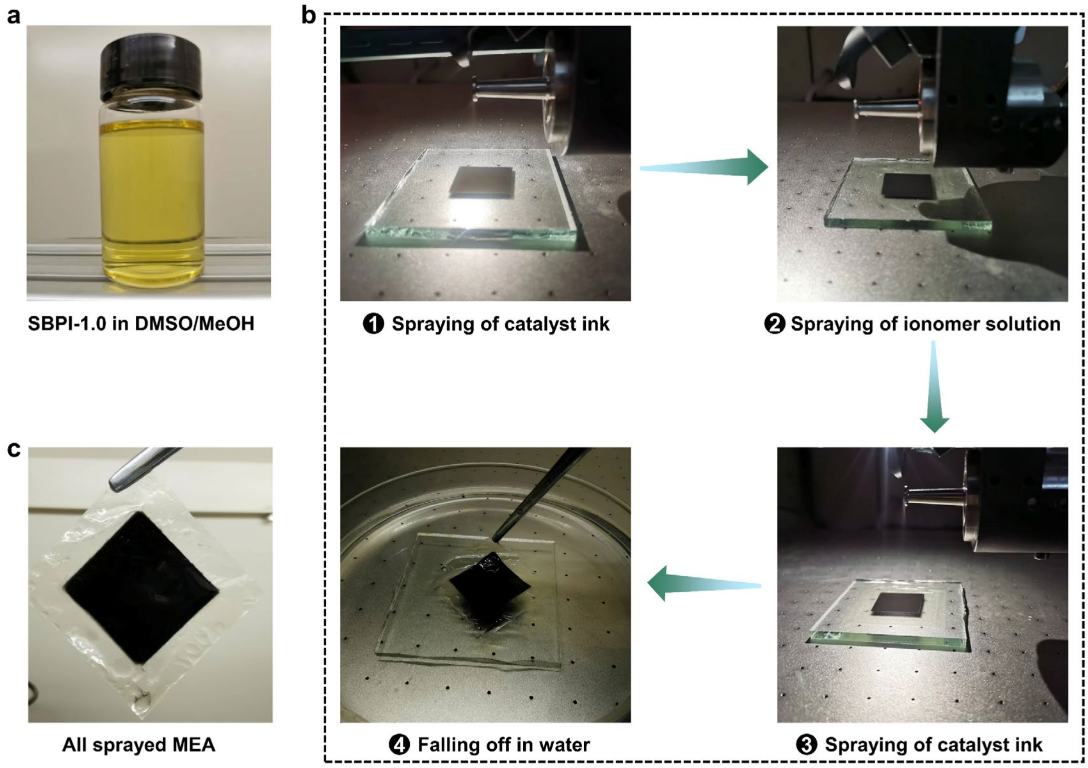

Fig. S2 Fabrication of AS-MEA. (a) 5 *wt%* SBPI-1.0 proton-conducting ionomer solution in DMSO/MeOH (*v*/*v* = 1:2). (b) Photos of the fabrication processes. Step 1: spraying the catalyst ink onto a glass plate to form a catalyst layer (catalyst loading can be controlled quantitatively). Step 2: spraying the proton-conducting ionomer solution onto the surface of the catalyst layer. Step 3: spraying the catalyst ink onto the surface of the PEM to form an MEA. Step 4: the MEA will naturally fall off from the glass plate after hydration in water. (c) Photo of the AS-MEA.

3. Scanning electron microscopy (SEM) characterization of the PEMs

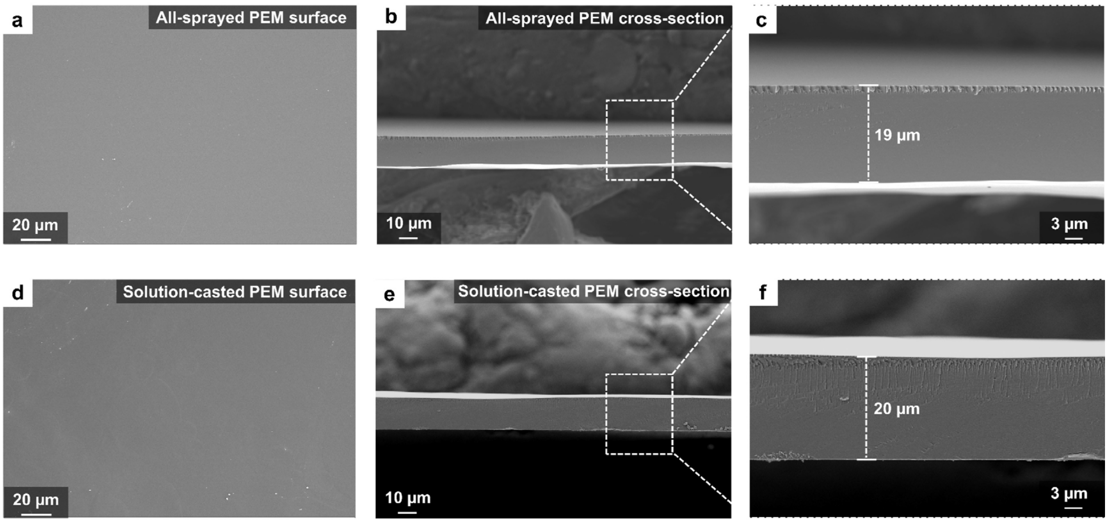

Fig. S3 SEM images. Surface SEM image of the (a) all-sprayed PEM, (d) solution-casted PEM. Cross-sectional SEM image of the (b-c) all-sprayed PEM, (e-f) solution-casted PEM.

4. Mechanical properties and polymer density of the PEMs

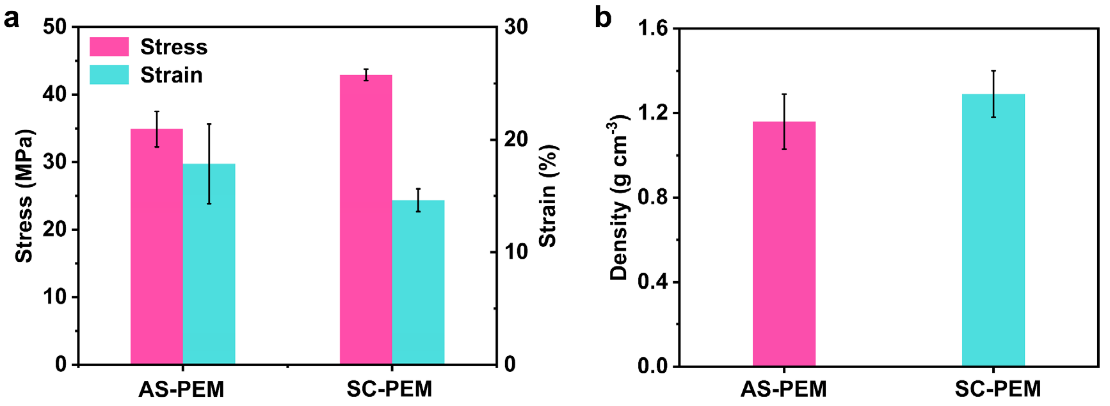

Fig. S4 (a) Mechanical properties including tensile strength and elongation at break of the AS- and SC-PEMs. (b) Density of the AS- and SC-PEMs.

5. Cross-sectional energy dispersive spectroscopy characterization

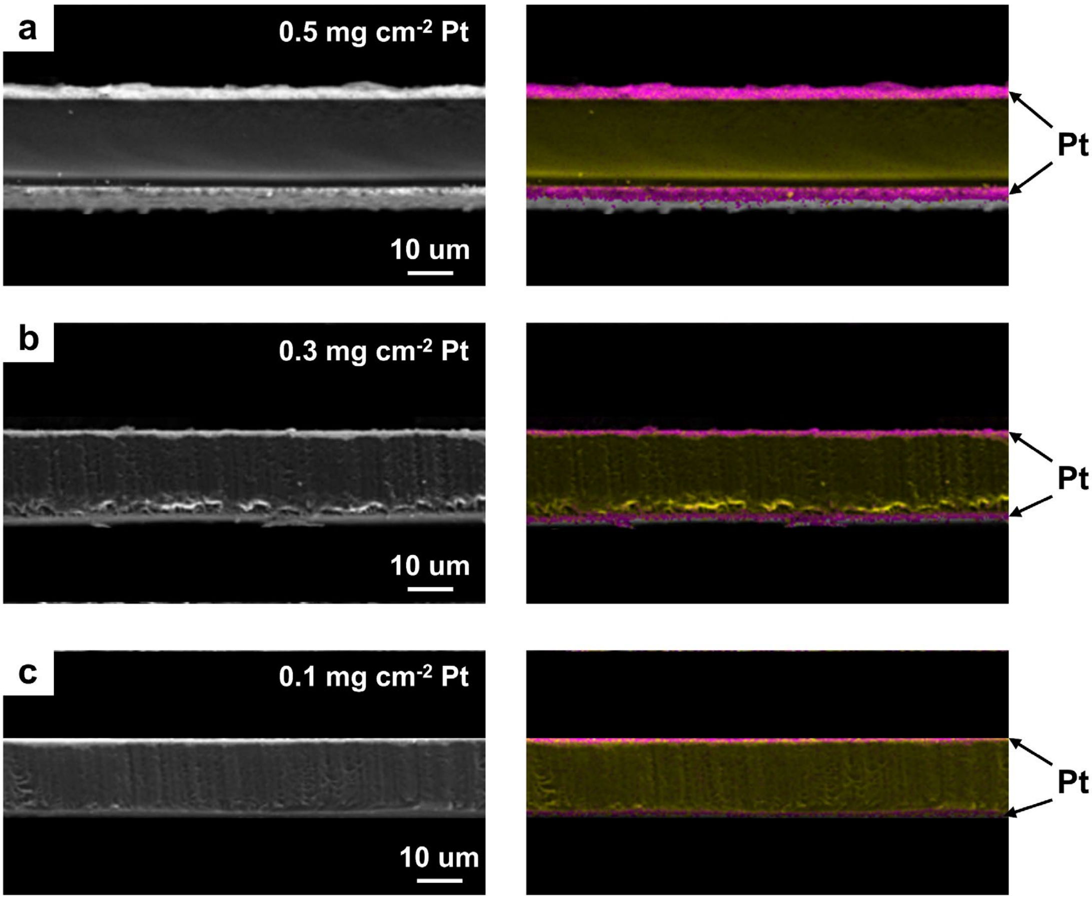

Fig. S5 Energy dispersive spectroscopy (EDS) characterization of the AS-MEAs. Cross-sectional EDS images and Pt element distribution of the AS-MEA with a Pt loading of (a) 0.5, (b) 0.3, and (c) 0.1 mg cm^{-2}.

6 Cross-sectional SEM characterization of the AS- and CCS-MEAs.

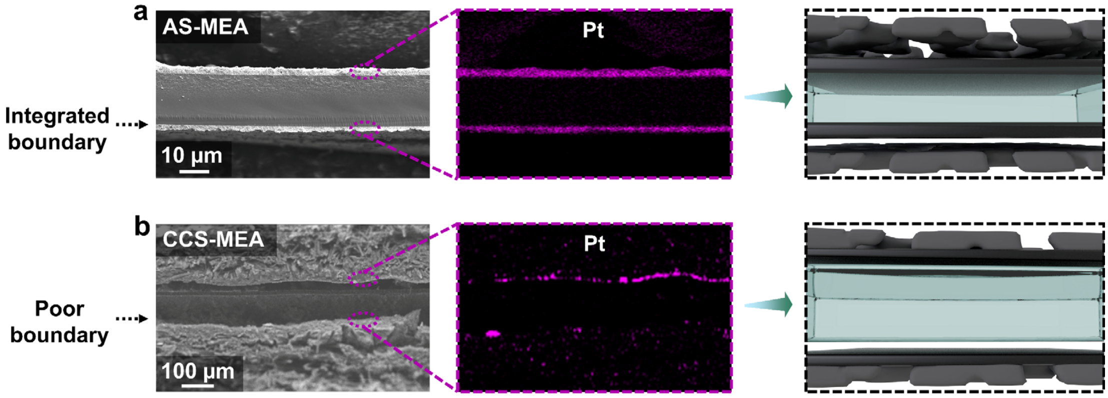

Fig. S6 Cross-sectional SEM images of the (a) AS-MEA, (b) CCS-MEA; and the corresponding platinum elemental mapping. For CCS-MEA, the cross-sectional SEM image was collected after the single-cell performance evaluation because only in this way we can get a whole MEA.

7. Fuel cell performance of the CCM-MEA

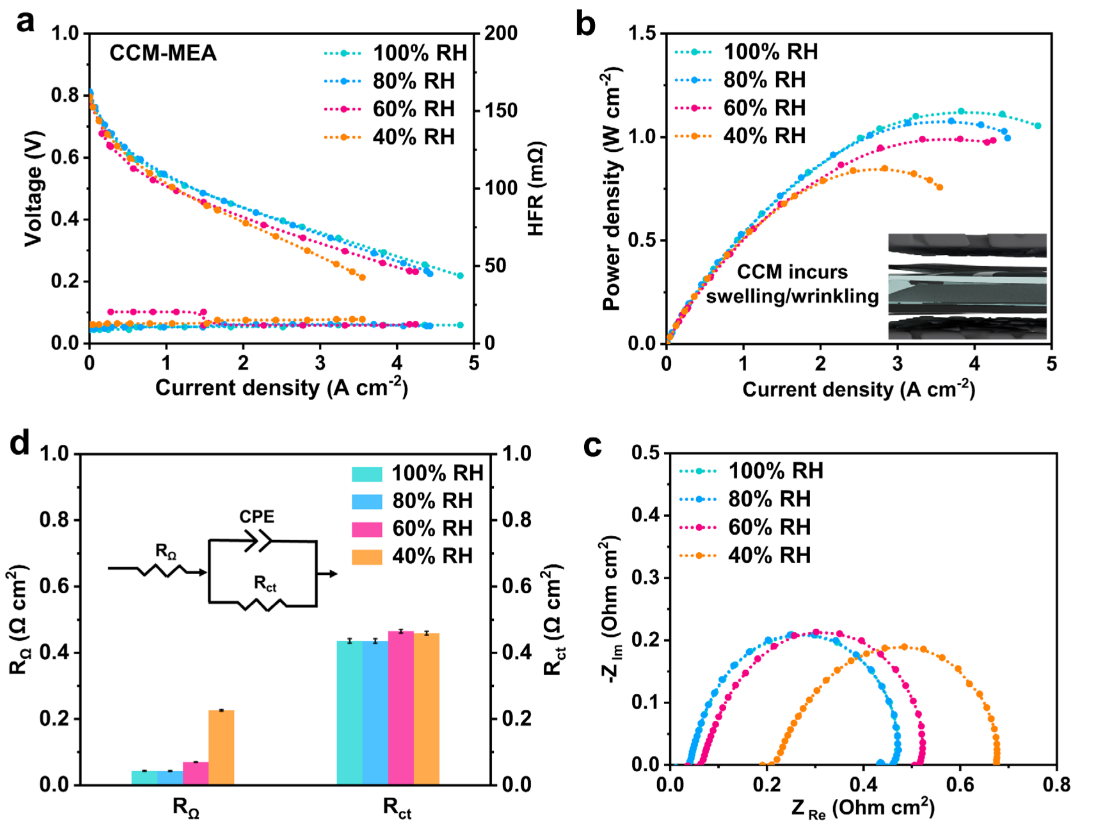

Fig. S7 Fuel cell performance of the CCM-MEA with pt loading of 0.5 mg cm^{-2}. (a) Current-voltage curves and HFR data. (b) Power density curves (the inserts represent the corresponding cross-sectional schematic of the CCM-MEA). (c) EIS spectra. (d) Ohmic resistance (R_Ω) and charge-transfer resistance (R_{ct}) values. The single-cell performance was evaluated at 70 °C with a low flow rate of 0.1 L min^{-1} H_2/O_2 and 0.1 MPa backpressure for the anode and cathode.

8. High-frequency resistances curves of the AS- and CCS-MEAs.

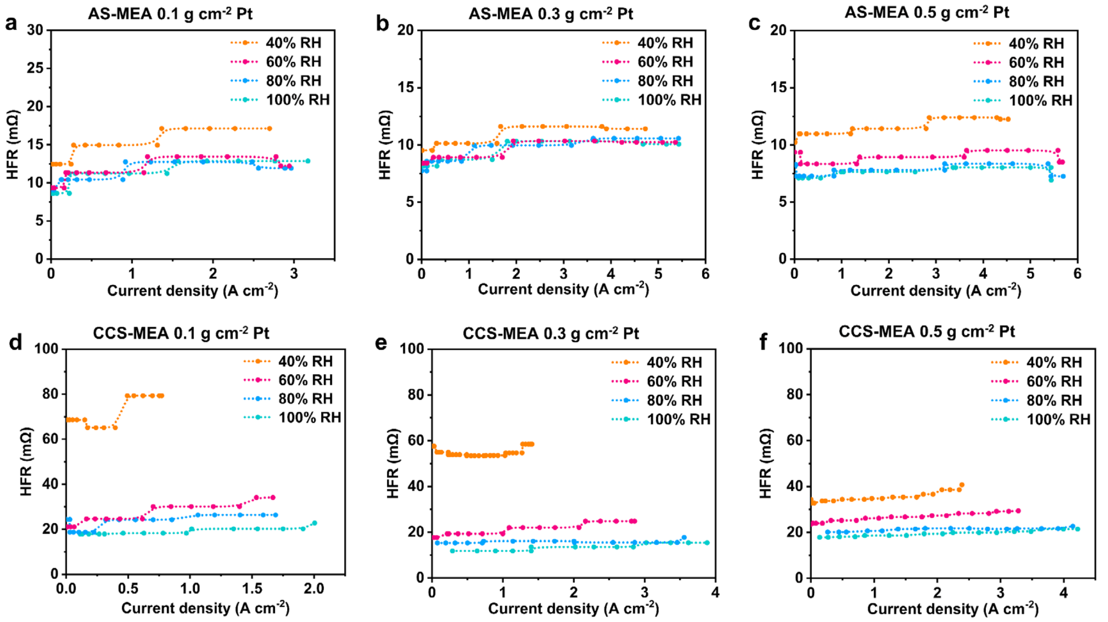

Fig. S8 High-frequency resistance (HFR) data. HFR curves of the AS-MEA with Pt loading of (a) 0.1 g cm^{-2}, (b) 0.3 g cm^{-2}, (c) 0.5 g cm^{-2}. HFR curves of the CCS-MEA with Pt loading of (d) 0.1 g cm^{-2}, (e) 0.3 g cm^{-2}, (f) 0.5 g cm^{-2}.

9. Electrochemical impedance spectra

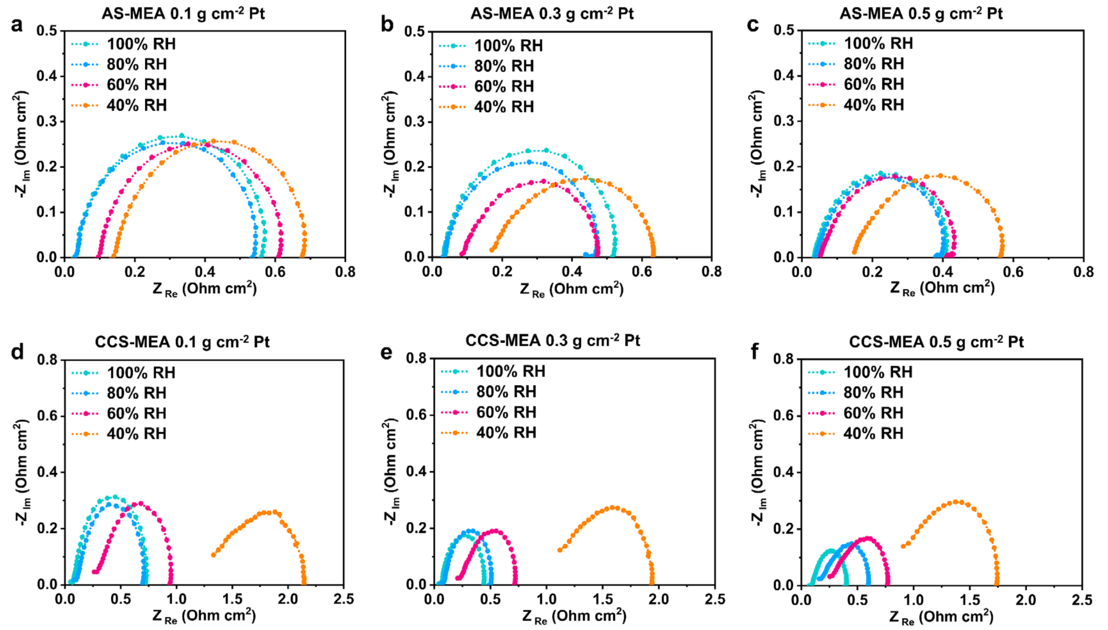

Fig. S9 Electrochemical impedance spectroscopy (EIS) characterization. EIS spectra of the AS-MEA with a Pt loading of (a) 0.1, (b) 0.3, (c) 0.5 mg cm^{-2} and the CCS-MEA with a Pt loading of (d) 0.1, (e) 0.3, (f) 0.5 mg cm^{-2} at different relative humidity (at a galvanostatic mode of 1 A and 0.1 L min^{-1} H_2/O_2).

10. H_2 cross-over of the AS-MEA before and after accelerated stress test.

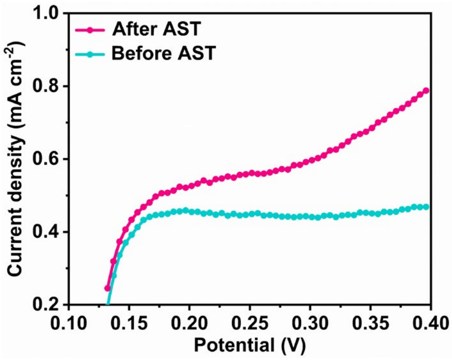

Fig. S10 Linear sweep voltammograms (LSVs) of the AS-MEA before and after the AST measurement.

References

1. W. Yu, Z. Ge, K. Zhang, X. Liang, X. Ge, H. Wang, M. Li, X. Shen, Y. Xu, L. Wu and T. Xu, *Ind. Eng. Chem. Res.*, 2022, **61**, 4329-4338.