

Supporting Information

Accurate Potentials of Hg/HgO Electrodes: Practical Parameters for Reporting Alkaline Water Electrolysis Overpotentials

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Experimental Details

Materials

Sodium hydroxide pellets ($\geq 99\%$, EMSURE[®]) and potassium hydroxide flakes (90%, Sigma Aldrich) were used in their as-received form. Ultra-pure deionized (DI) water (approximately 17 M Ω resistance) was used for preparing all aqueous solutions.

Hg/HgO Electrode Calibration

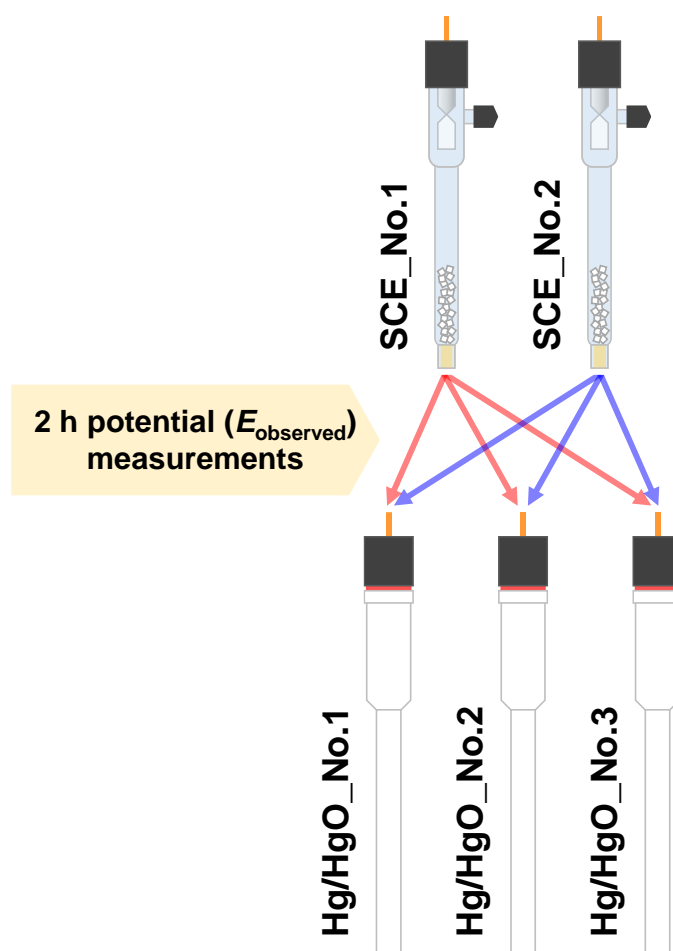
By using a True RMS multimeter (model: 175, Fluke Corporation), the potentials (E_{observed}) of three Hg/HgO reference electrodes (model: CHI 152, CH Instruments, Inc.; model: RE-1A, Shanghai Yueci Electronic Technology Co., Ltd.) were measured against each saturated calomel electrodes (SCEs, model: CHI 150, CH Instruments, Inc.) in 20 mL of an external alkaline electrolyte (see the right side of Figure 1 and Scheme S1). To maintain the temperature of the experimental system at 25 °C, an electrochemical cell was placed in a digital water bath (IVYX Scientific) (see Figure S2). Notably, for the internal solution and external electrolyte, the alkaline solutions with the same constituents at the same concentrations were used. The above-mentioned potential measurements were performed for six different internal solution cases (i.e., 0.1, 0.5, and 1 M NaOH/KOH). For each potential measurement, we spent 2 h to record a stabilized potential value (E_{observed}).

Hg/HgO Electrode Internal Solution Exchange

A Hg/HgO electrode main body (see Figure S9a) was taken out from a Teflon outer body (see Figure 1). The as-removed Hg/HgO electrode main body was rinsed with DI water and the desired internal alkaline solution. The inside of the Teflon out body was washed with DI water four times and further washed with the desired internal alkaline solution three times. Subsequently, the reassembled Hg/HgO electrode main body and the Teflon outer body were filled with the desired internal solution. The as-prepared Hg/HgO electrode was kept at room temperature for 24 h at minimum in order to stabilize its potential.

Cotton Absorbent Analysis

A Hg/HgO main body pre-immersed in 1 M KOH was rinsed with DI water, dried at room temperature to improve its water absorbability, and then immersed in 4 mL of DI water for 50 h (see Figure S9b). Afterward, a Hg/HgO main body was taken out from the vial and rinsed with DI water. A small portion of a cotton absorbent was collected from the as-immersed Hg/HgO main body and loaded on a holder using carbon tape. The as-prepared sample was analyzed by using a Quanta 650 environmental scanning electron microscope (ESEM, FEI) with an energy-dispersive X-ray spectroscopy (EDX) detector (XFlash 6|10, Bruker Nano GmbH).



Scheme S1. Experimental design for measuring Hg/HgO electrode potentials. For each of the six internal solution cases (i.e., 0.1, 0.5, and 1 M NaOH/KOH), two means of triplicate $E_{\text{Hg/HgO}(x \text{ M MOH})}^{\text{real}}$ values and two corresponding standard deviations were measured using two SCEs and three Hg/HgO electrodes.

Calculation Details

Liquid Junction Potential (Solution A | Solution B) Calculations²

The potentials of different liquid junctions were calculated through the Henderson equation (see equation S1). Equivalent limiting ionic conductivity (λ_0) values necessary for this calculation are listed in Table S2. Additionally, the concentration of a saturated KCl aqueous solution was set at 4.6 M.¹

Henderson equation:

$$E_{\text{LJP}} = \frac{RT}{F} \frac{(U_A - V_A) - (U_B - V_B)}{(U'_A + V'_A) - (U'_B + V'_B)} \ln \frac{U'_A + V'_A}{U'_B + V'_B} \quad (\text{S1})$$

$$U = \sum C_+ \lambda_+^0$$

$$V = \sum C_- \lambda_-^0$$

$$U' = \sum C_+ \lambda_+^0 |z_+|$$

$$V' = \sum C_- \lambda_-^0 |z_-|$$

E_{LJP} : Liquid junction potential

C_+ : Cation concentration (M)

C_- : Anion concentration (M)

λ_+^0 : Limiting cationic conductivity ($\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$)

λ_-^0 : Limiting anionic conductivity ($\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$)

z : Ion valence

Two-Sample *t*-Test: Comparison of Two Measured Potential Means³

Two potential [$E_{\text{Hg/HgO}(x \text{ M MOH})}^{\text{real}}$] means (see Table 1) obtained using two different SCEs (Nos. 1 and 2) were statistically compared.

Pooled standard deviation (s_{pooled}):

$$s_{\text{pooled}} = \sqrt{\frac{s_1^2(n_1-1) + s_2^2(n_2-1)}{n_1+n_2-2}} \quad (\text{S2})$$

Statistic t value (t_{calc}):

$$t_{\text{calc}} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{\text{pooled}}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}} \quad (\text{S3})$$

As seen in Table S3, since all the as-obtained t_{calc} values are smaller than the critical t value (2.776, see Ref. 3) at 95% confidence level and 4 degrees of freedom, two sets of the Hg/HgO electrode potentials obtained using two different SCEs (Nos. 1 and 2) are not significantly different for all the internal solution cases.

Comparison of a Measured Potential Mean with a Calculated Potential Value³

Experimental and calculated potential [$E_{\text{Hg/HgO}(x \text{ M MOH})}^{\text{real}}$] values were statistically compared.

Confidence interval:

$$\text{Confidence interval} = \bar{x} \pm \frac{ts}{\sqrt{n}} \quad (\text{S4})$$

t : Student's t value (4.303 at 95% confidence level and 2 degrees of freedom)

Supporting Tables

Table S1. Essential parameters for calculating the potential of the Hg/HgO electrodes with different internal solutions^a

	Hg/HgO electrode potential calculation parameters					
	Internal solution					
	0.1 M NaOH	0.5 M NaOH	1 M NaOH	0.1 M KOH	0.5 M KOH	1 M KOH
T (°C)	25	25	25	25	25	25
pH ^a	12.895	13.547	13.847	12.899	13.568	13.890
γ_{OH^-} ^a	0.782	0.691	0.677	0.789	0.726	0.748
$a_{\text{H}_2\text{O}}$ ^a	0.9966	0.9832	0.9655	0.9966	0.9829	0.9642

^apH, the activity coefficient of OH⁻ (γ_{OH^-}), and the activity of H₂O ($a_{\text{H}_2\text{O}}$) values were calculated using the Excel spreadsheet tool created by Hausmann *et al.*⁴

Table S2. Equivalent limiting ionic conductivity (λ_0) values at infinite dilution (25 °C) from Ref. 5

Ion	λ_0 (S·cm ² ·mol ⁻¹)
Na ⁺	50.08
K ⁺	73.48
OH ⁻	198
Cl ⁻	76.31

Table S3. Two-sample t -test results: The s_{pooled} and t_{calc} values calculated from equations (S2) and (S3)

	Statistical analysis results	
Internal solution	s_{pooled} value	t_{calc} value
1 M NaOH	1.077	1.251
1 M KOH	2.455	0.349
0.5 M NaOH	1.557	0.786
0.5 M KOH	1.700	0.792
0.1 M NaOH	1.657	0.148
0.1 M KOH	2.089	0.059

Supporting Figures

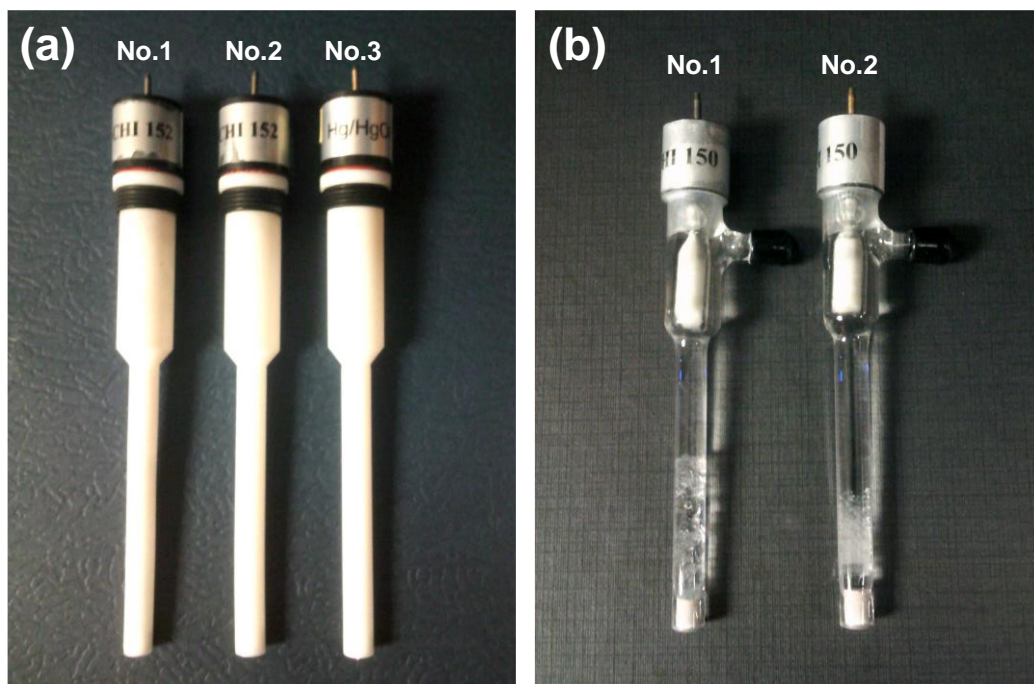


Figure S1. Digital photographs of (a) Hg/HgO electrodes and (b) saturated calomel electrodes.

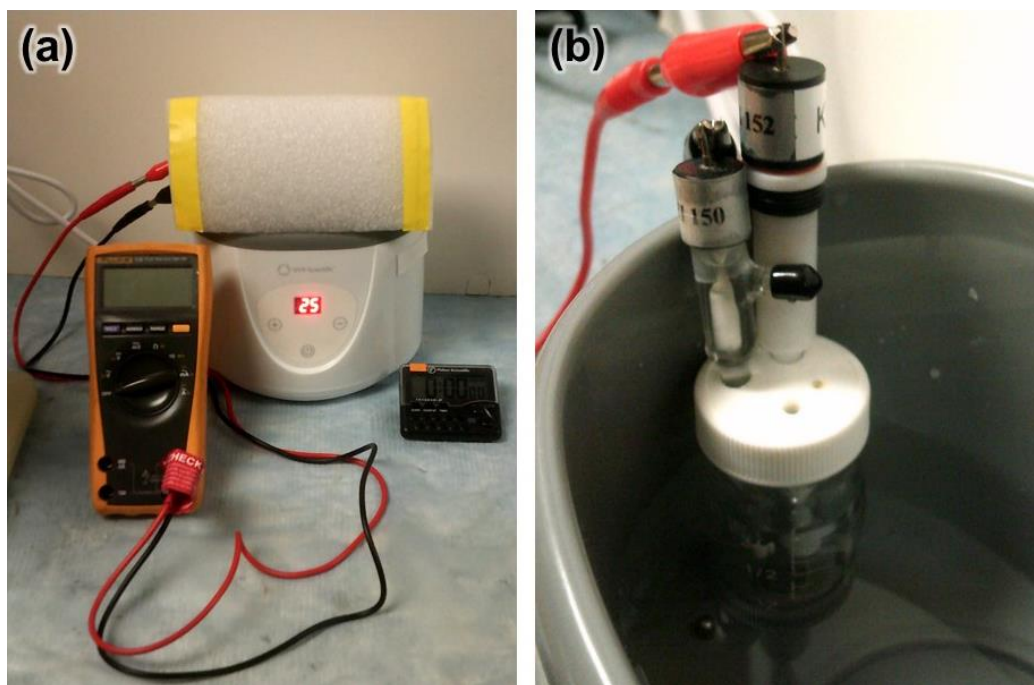


Figure S2. Digital photographs of (a) the entire experimental setup and (b) the electrochemical cell for the potential difference measurement (Hg/HgO electrodes vs. SCEs).

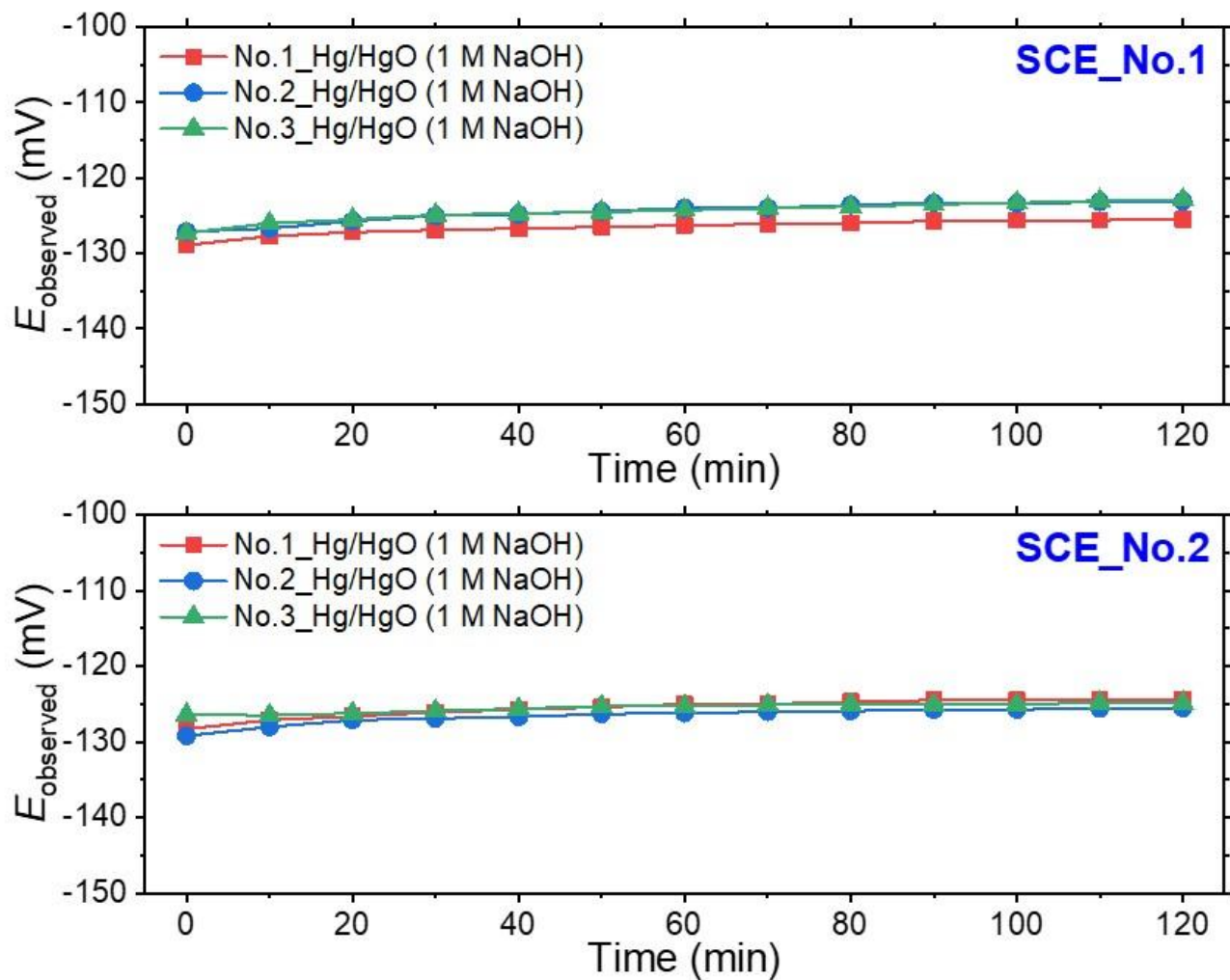


Figure S3. Time-potential (mV vs. SCE) curves of the three Hg/HgO (1 M NaOH) electrodes (Nos. 1–3). Each of the two SCEs (Nos. 1 and 2) was used to measure the three Hg/HgO electrode potentials.

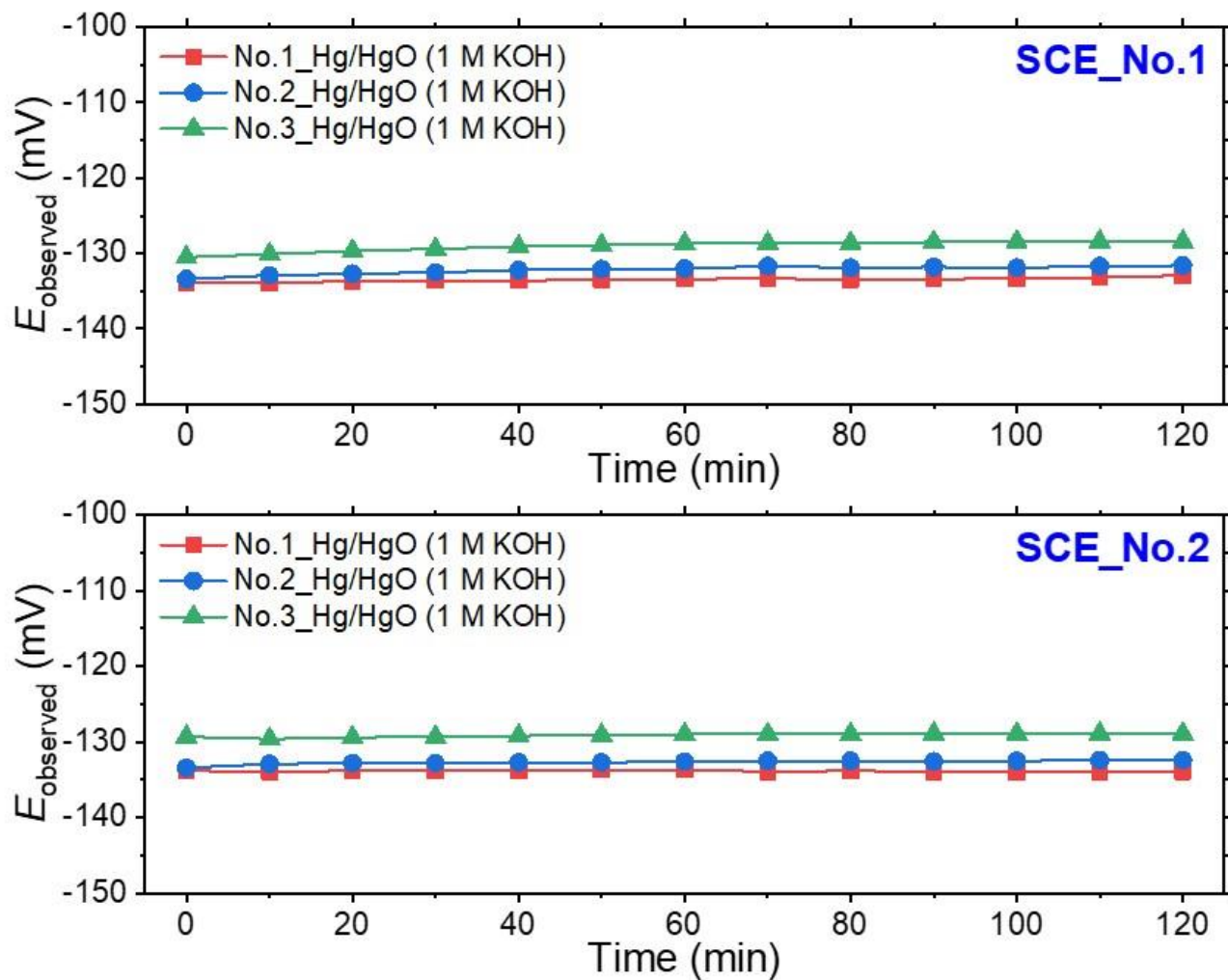


Figure S4. Time-potential (mV vs. SCE) curves of the three Hg/HgO (1 M KOH) electrodes (Nos. 1–3). Each of the two SCEs (Nos. 1 and 2) was used to measure the three Hg/HgO electrode potentials.

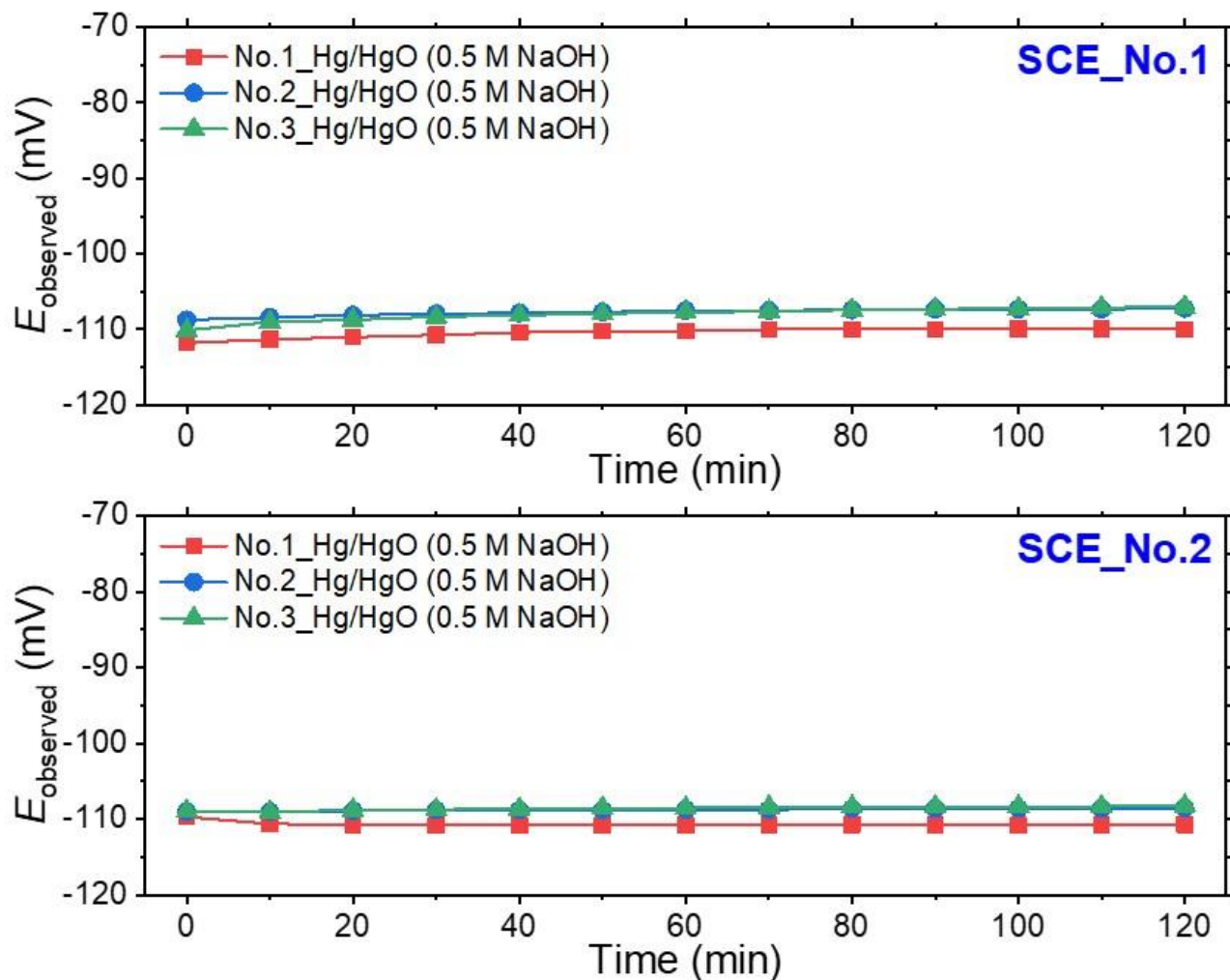


Figure S5. Time-potential (mV vs. SCE) curves of the three Hg/HgO (0.5 M NaOH) electrodes (Nos. 1–3). Each of the two SCEs (Nos. 1 and 2) was used to measure the three Hg/HgO electrode potentials.

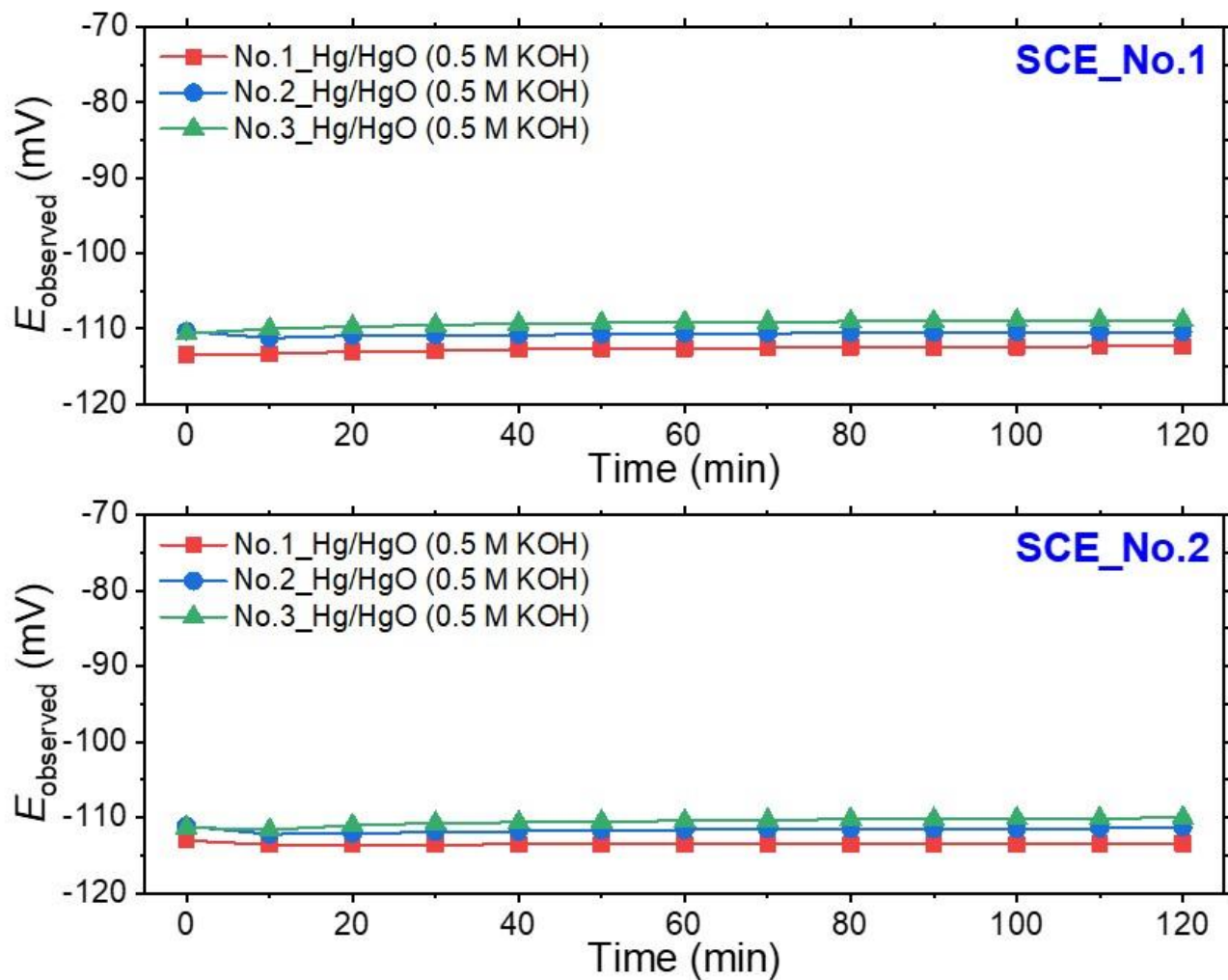


Figure S6. Time-potential (mV vs. SCE) curves of the three Hg/HgO (0.5 M KOH) electrodes (Nos. 1–3). Each of the two SCEs (Nos. 1 and 2) was used to measure the three Hg/HgO electrode potentials.

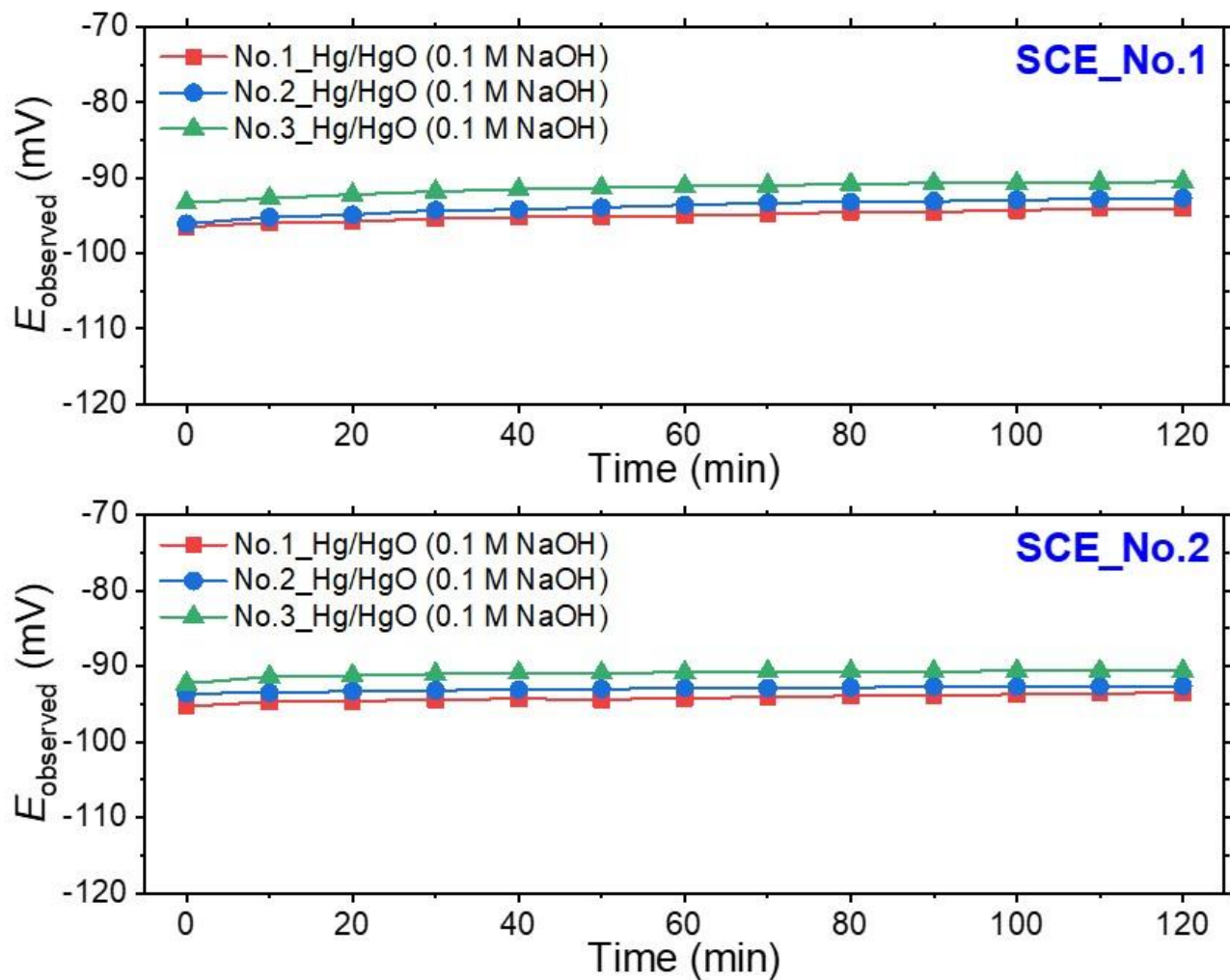


Figure S7. Time-potential (mV vs. SCE) curves of the three Hg/HgO (0.1 M NaOH) electrodes (Nos. 1–3). Each of the two SCEs (Nos. 1 and 2) was used to measure the three Hg/HgO electrode potentials.

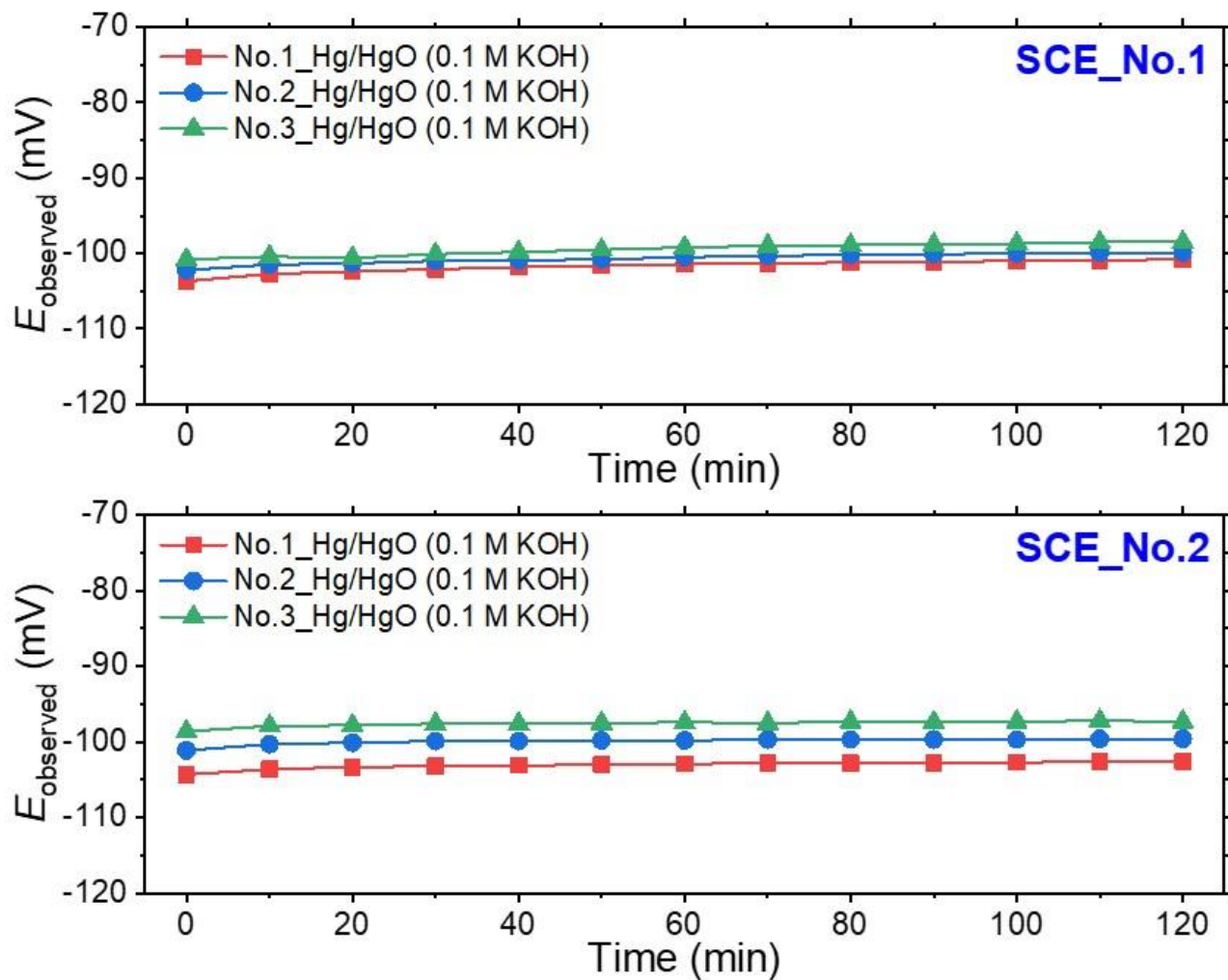


Figure S8. Time-potential (mV vs. SCE) curves of the three Hg/HgO (0.1 M KOH) electrodes (Nos. 1–3). Each of the two SCEs (Nos. 1 and 2) was used to measure the three Hg/HgO electrode potentials.

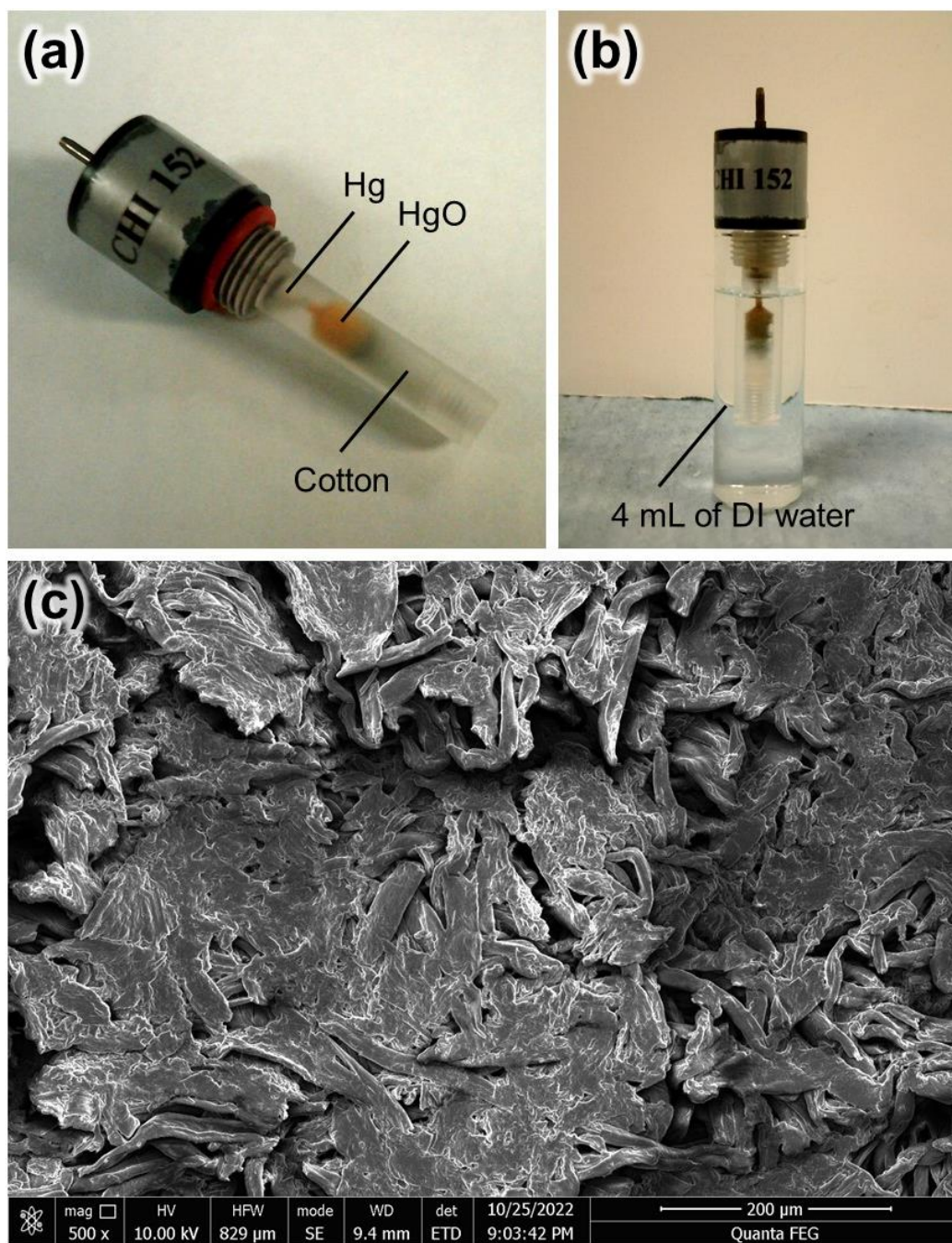


Figure S9. (a) Digital photographs of a Hg/HgO electrode main body and (b) an experimental setup for dipping the Hg/HgO electrode main body in DI water for 50 h. (c) SEM image of a cotton absorbent after the 50 h DI water dipping test.

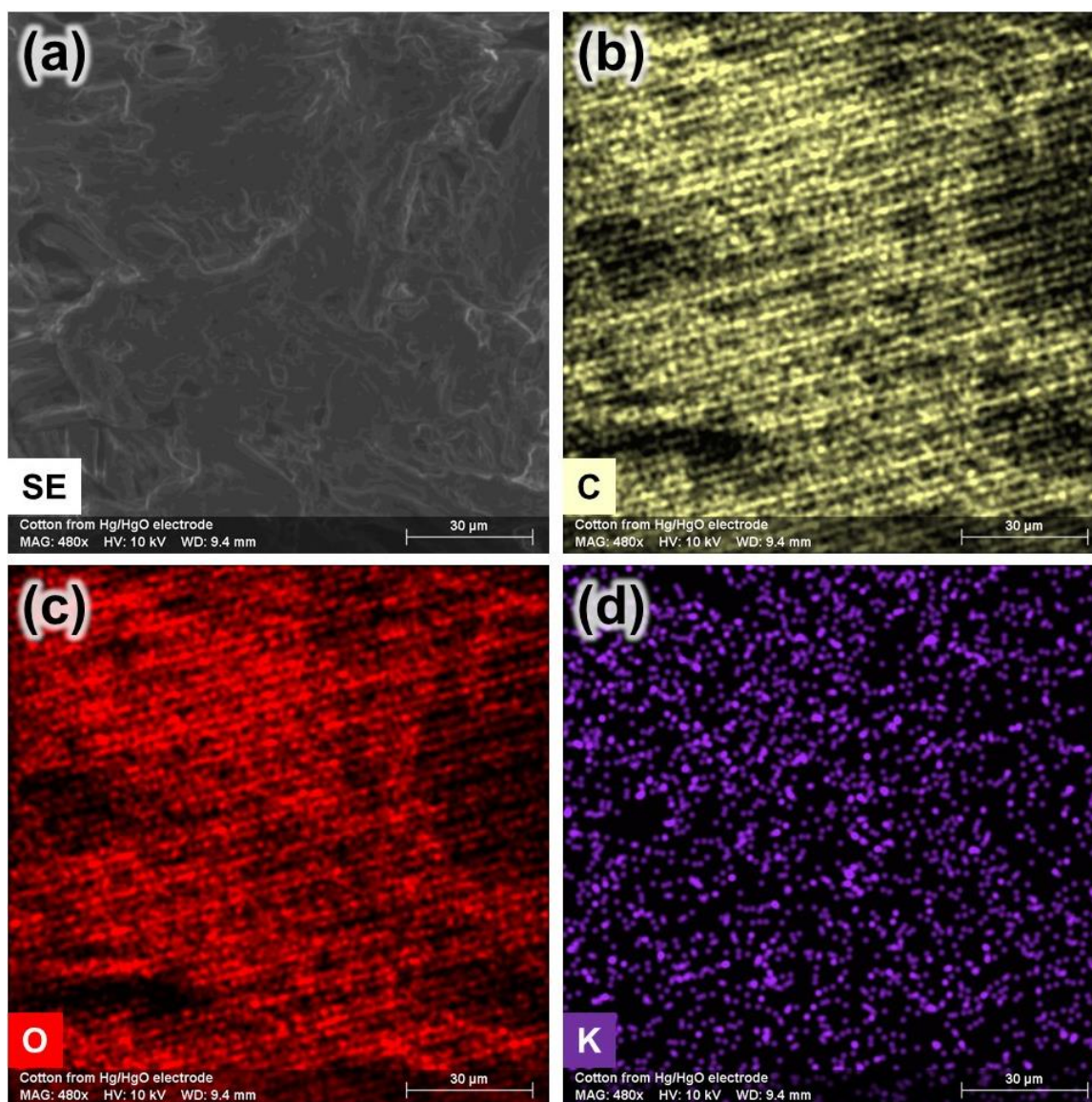


Figure S10. SEM-EDX elemental mapping images of a cotton absorbent after the 50 h DI water dipping test.

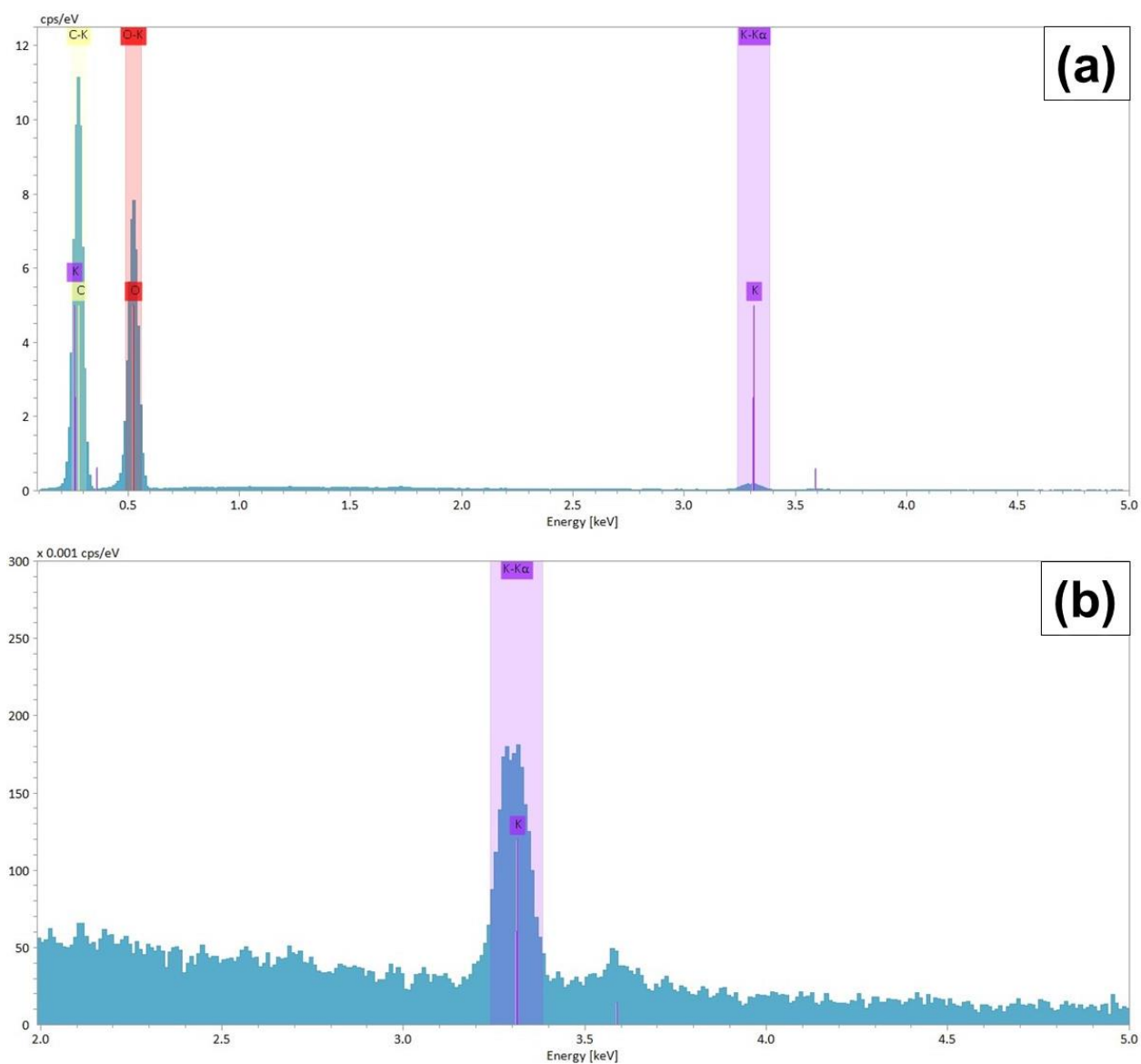


Figure S11. (a) Entire and (b) magnified EDX spectra of a cotton absorbent after the 50 h DI water dipping test. These data correspond to Figure S10.

References

- (1) Park, R. M. A Guide to Understanding Reference Electrode Readings. *Mater. Perform.* **2009**, 48 (9), 32–36.
- (2) Bates, R. G. *Determination of pH*, 2nd ed.; A Wiley-Interscience Publication: New York, New York, 1973.
- (3) Harris, D. C. *Quantitative Chemical Analysis*, 8th ed.; Clancy Marshall: New York, New York, 2010.
- (4) Hausmann, J. N.; Traynor, B.; Myers, R. J.; Driess, M.; Menezes, P. W. The pH of Aqueous NaOH/KOH Solutions: A Critical and Non-Trivial Parameter for Electrocatalysis. *ACS Energy Lett.* **2021**, 6 (10), 3567–3571. <https://doi.org/10.1021/acsenerylett.1c01693>.
- (5) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 72nd ed.; CRC Press, Inc., 1991.