Electronic Supporting Information

# Preparation and application of Cu-doped antimony electrode to improve the performance of pH measurement in seawater

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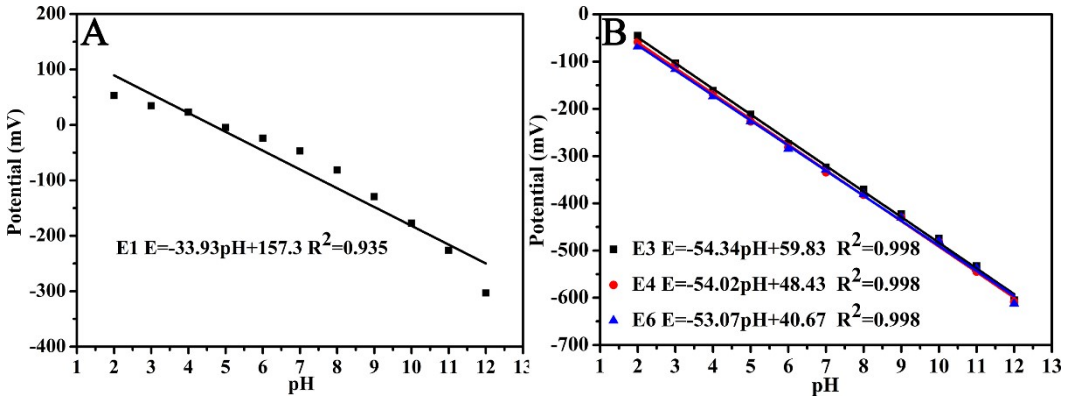


**Figure S1** (A) Response curve of E1 electrode in the pH range of 2-12; (B) Response curve of E3,E4 and E6 electrodes in the pH range of 2-12

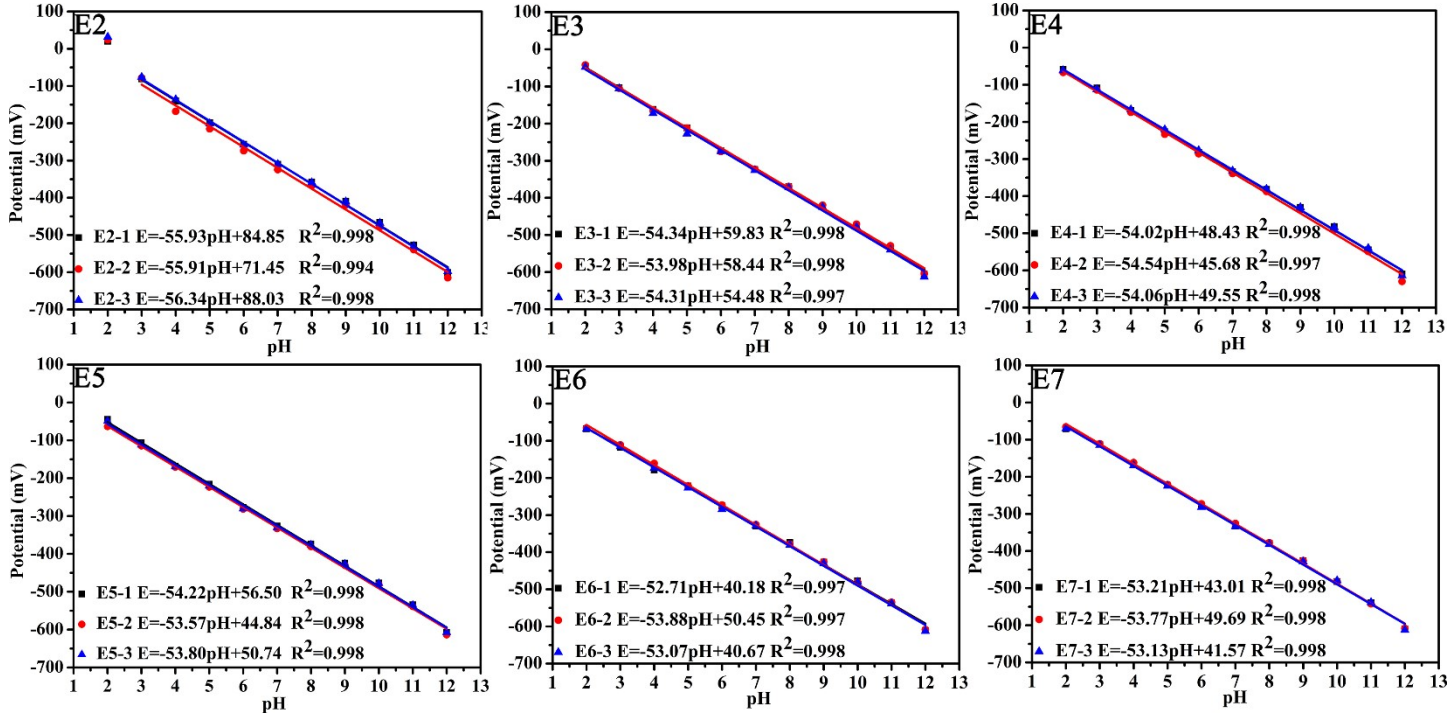


**Figure S2** Preparation using the same method, pH response performance of electrodes from different batches

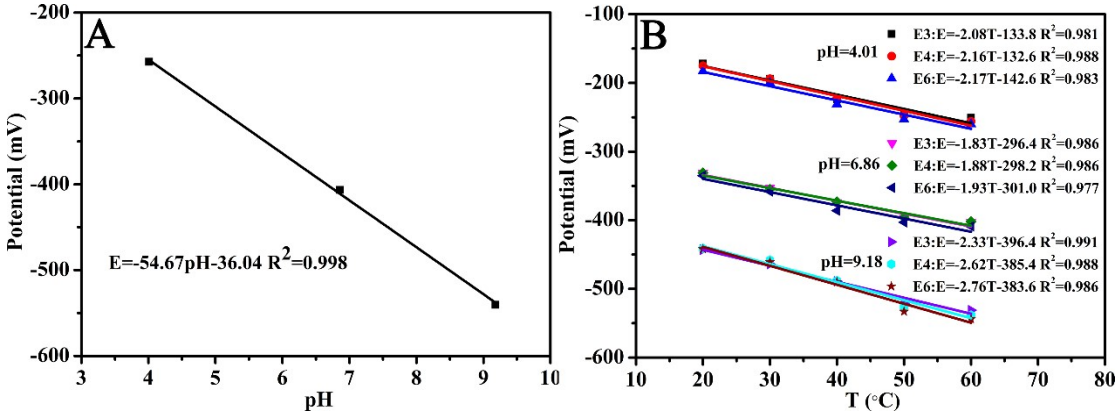


**Figure S3** (A) The pH response curve of E5 electrode at 60°C; (B) Temperature coefficients of E3, E4 and E6 electrodes under acidic (pH=4.01), neutral (pH=6.86) and alkaline (pH=9.18) conditions

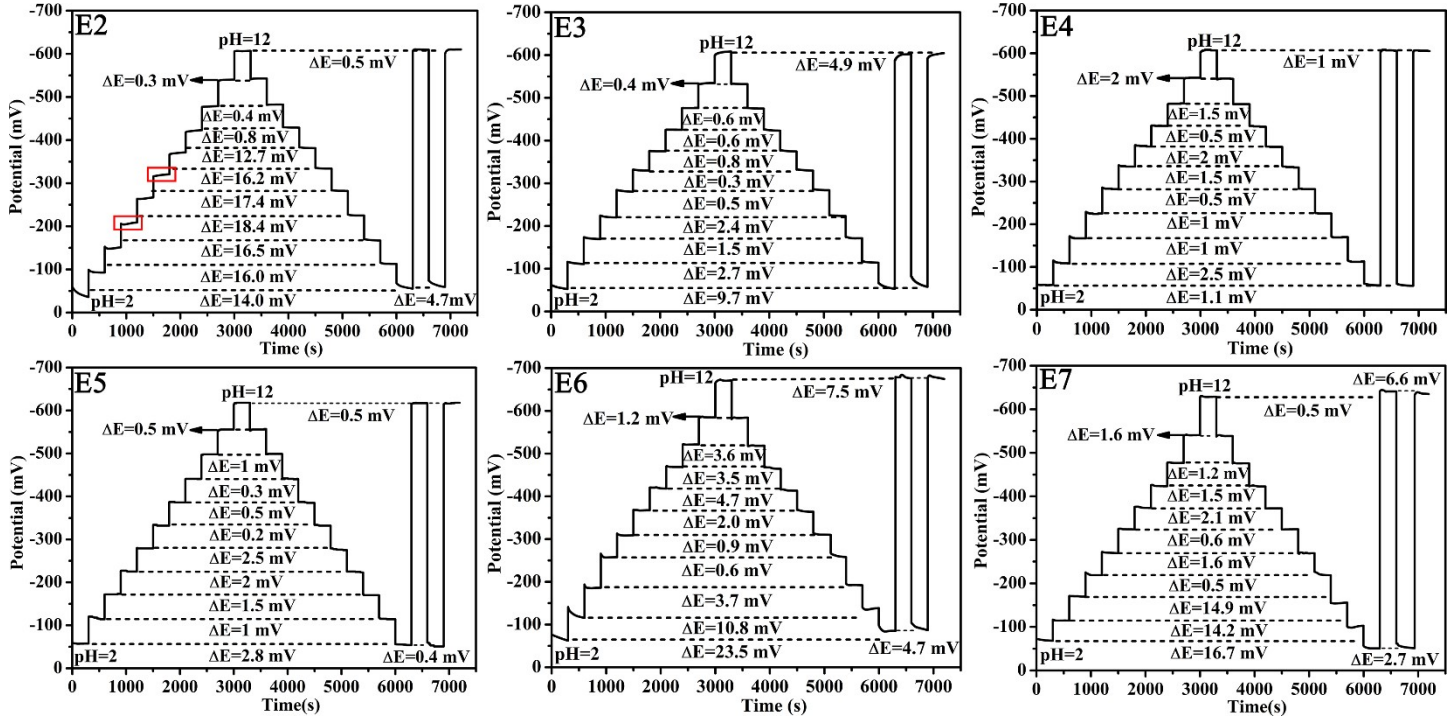


**Figure S4** Reversibility and hysteresis of different electrodes in Britton Robinson buffer solution (pH=2-12-2)

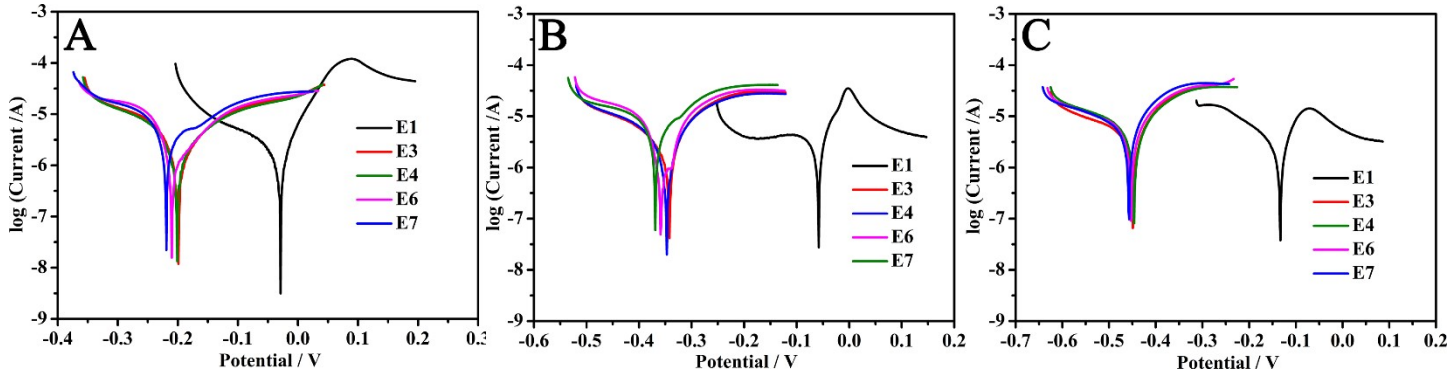


**Figure S5** Polarization curves of E1, E3, E4, E6 and E7 electrodes in standard buffer solutions with pH=4.01(A), 6.86(B), and 9.18(C)

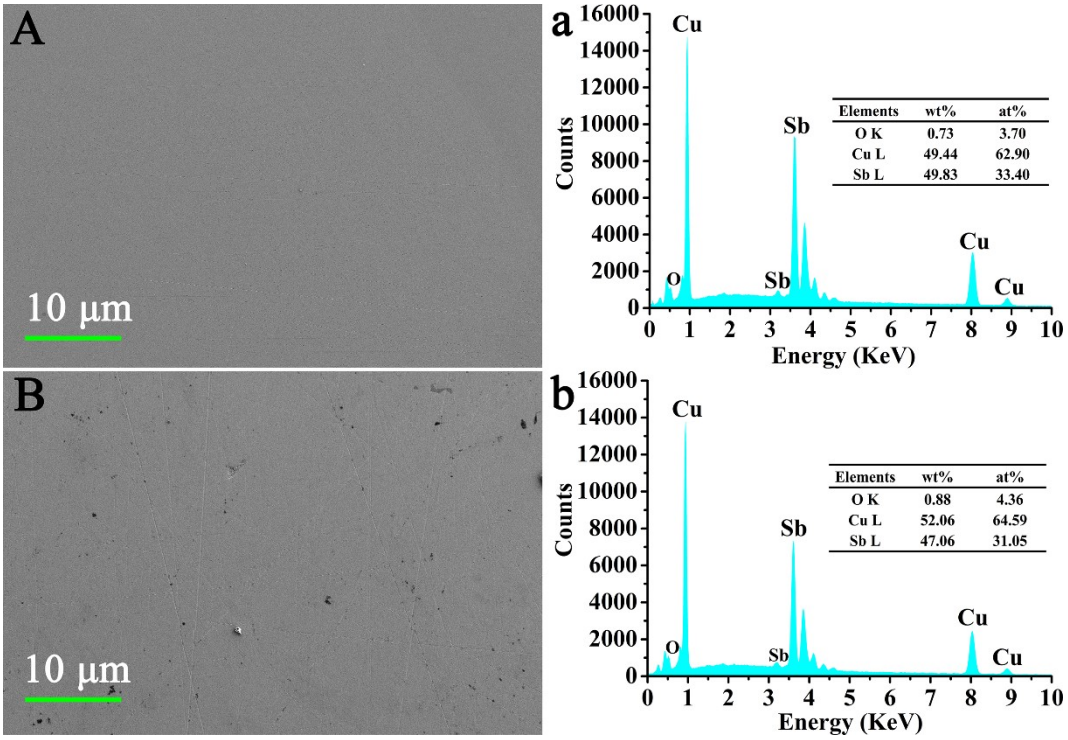


**Figure S6** The SEM images and EDS analysis of the E1 electrode surface before and after the electrochemical testing: (A) The SEM images of the E1 electrode surface before the electrochemical testing; (a) The corresponding EDS spectrum and the insert table was the EDS analysis results of the E1 electrode surface before the electrochemical testing; (B) The SEM images of the E1 electrode surface after the electrochemical testing; (b) The corresponding EDS spectrum and the insert table was the EDS analysis results of the E1 electrode surface after the electrochemical testing

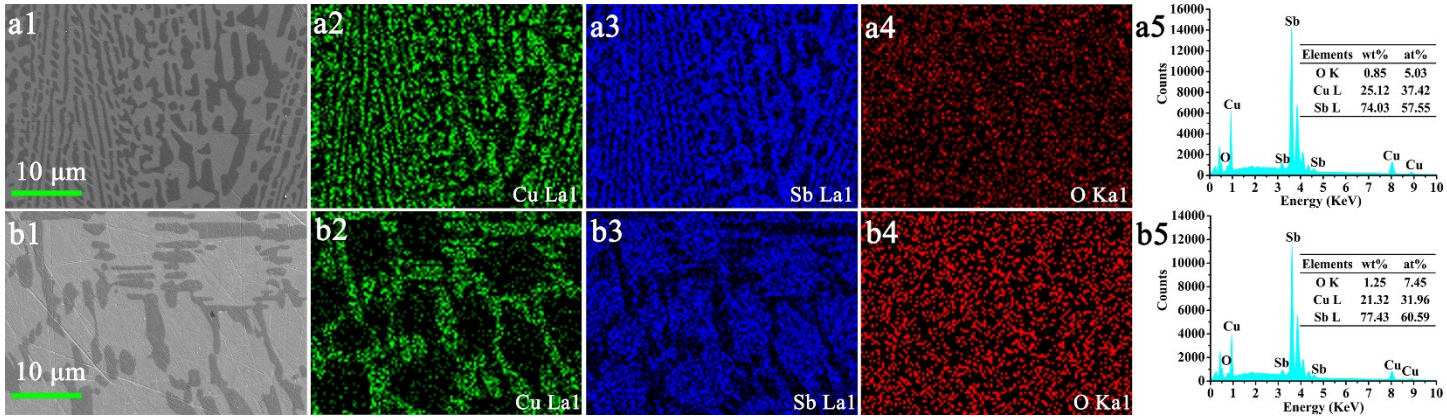


**Figure S7** The SEM images and EDS analysis of the E4 and E5 electrodes surface before the electrochemical testing: (a1, b1) The SEM images of the E4 and E5 electrodes surface before the electrochemical testing, respectively; (a2, b2) The copper element distribution map of the E4 and E5 electrodes surface before the electrochemical testing, respectively; (a3, b3) The antimony element distribution map of the E4 and E5 electrodes surface before the electrochemical testing, respectively; (a4, b4) The oxygen element distribution map of the E4 and E5 electrodes surface before the electrochemical testing, respectively; (a5, b5) The corresponding EDS spectrum of the mapping area and the insert table was the EDS analysis results of the E4 and E5 electrodes surface before the electrochemical testing, respectively

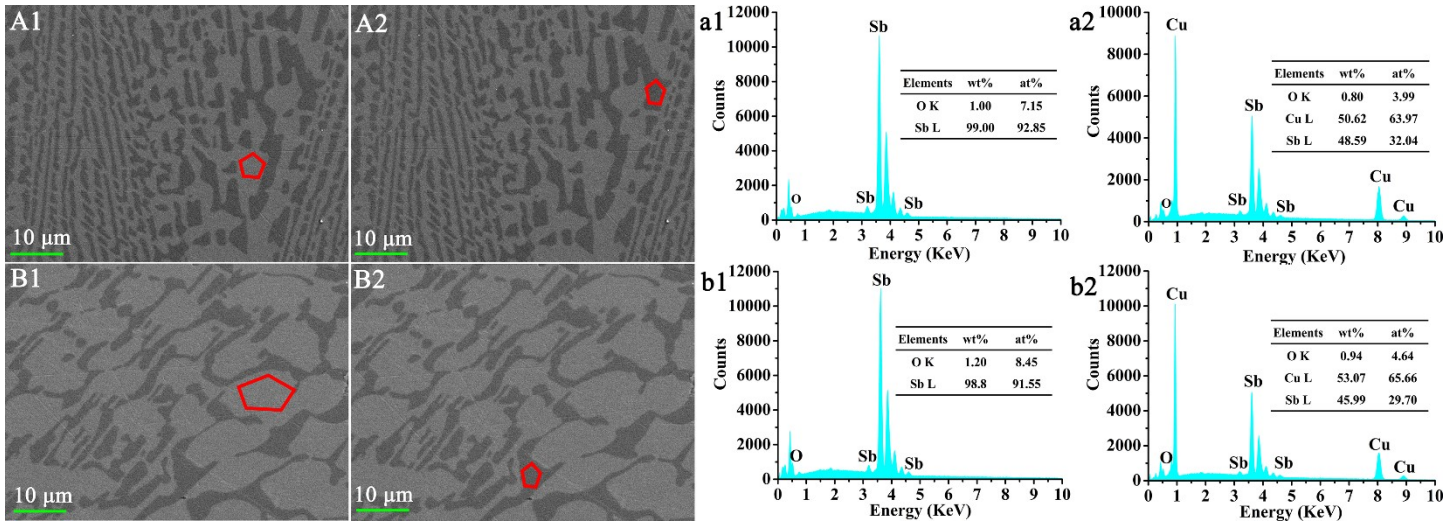


**Figure S8** The EDS point analysis of the E3 and E4 electrodes before the electrochemical testing: (A1, A2) the SEM image of the E4 electrode; (a1, a2) The EDS spectra corresponding to the red areas of A1 and A2, respectively and the insert tables were the EDS analysis results; (B1, B2) the SEM image of the E3 electrode; (b1, b2) The EDS spectra corresponding to the red areas of B1 and B2, respectively and the insert tables were the EDS analysis results

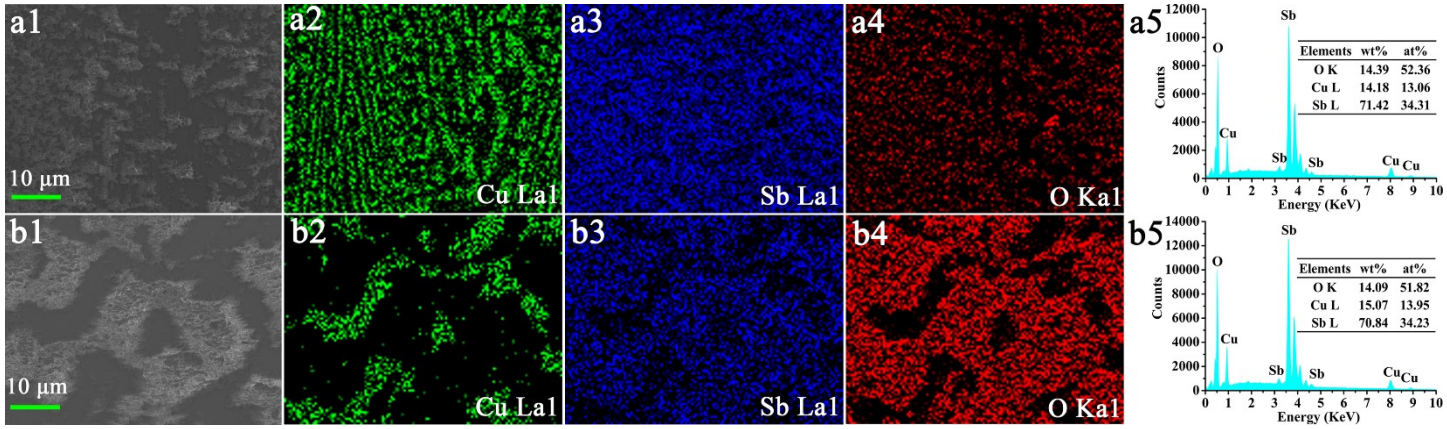


**Figure S9** The SEM images and EDS analysis of the E4 and E5 electrodes surface after the electrochemical testing: (a1, b1) The SEM images of the E4 and E5 electrodes surface after the electrochemical testing, respectively; (a2, b2) The copper element distribution map of the E4 and E5 electrodes surface after the electrochemical testing, respectively; (a3, b3) The antimony element distribution map of the E4 and E5 electrodes surface after the electrochemical testing, respectively; (a4, b4) The oxygen element distribution map of the E4 and E5 electrodes surface after the electrochemical testing, respectively; (a5, b5) The corresponding EDS spectrum of the mapping area and the insert table was the EDS analysis results of the E4 and E5 electrodes surface after the electrochemical testing, respectively

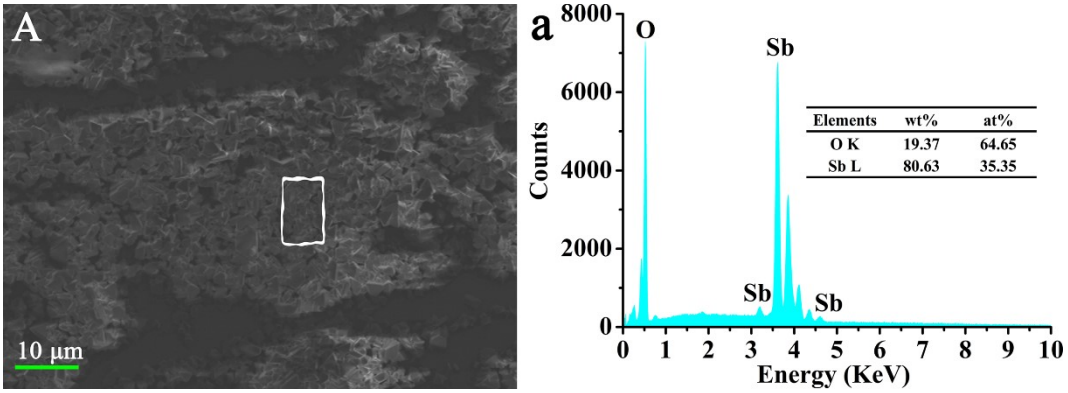


**Figure S10** The EDS point analysis of the E5 electrode after the electrochemical testing: (A) The SEM image of the E5 electrode; (a) The EDS spectra corresponding to the White box area of Fig. S5, A, and the insert tables were the EDS analysis results

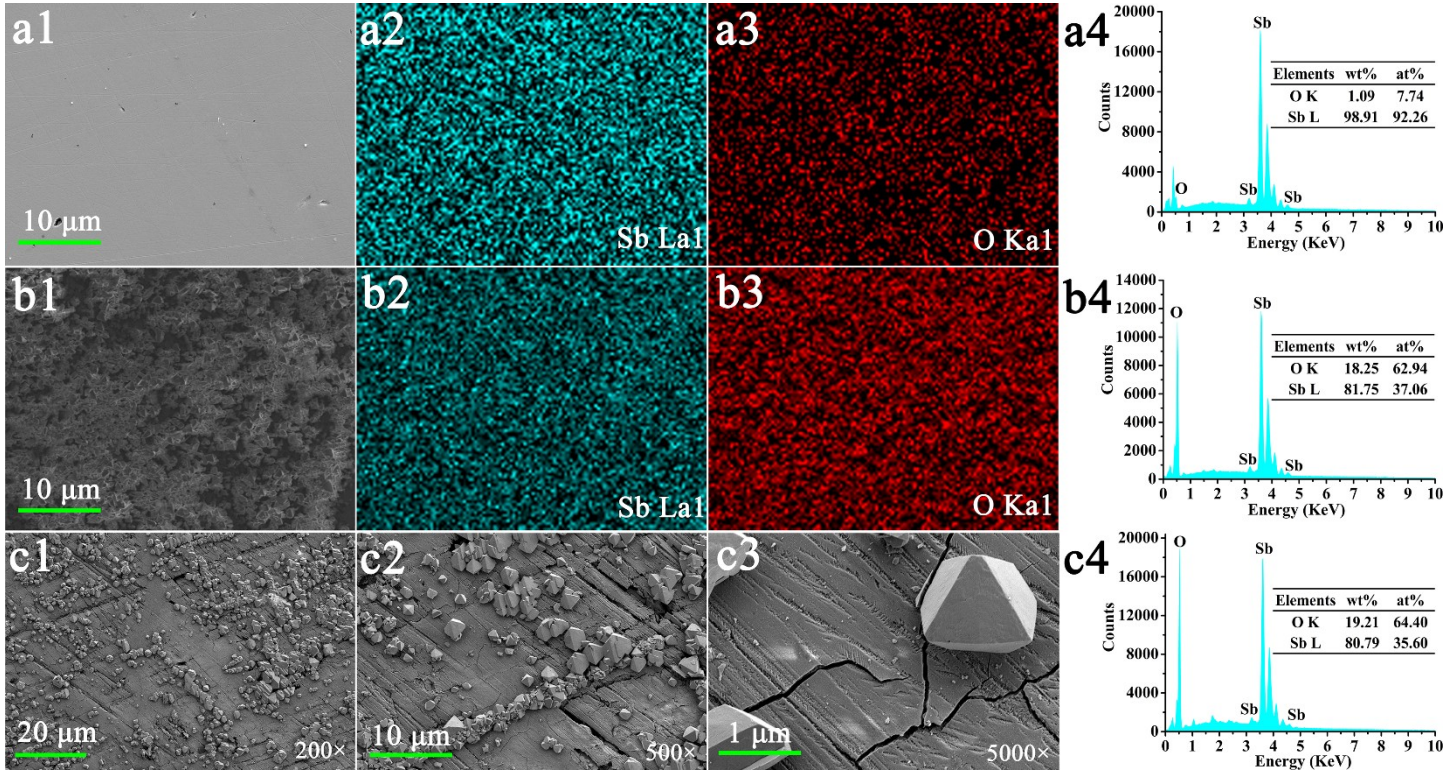


**Figure S11** The EDS analysis of the E7 electrode before (a1-a4) and after (b1-b4) the electrochemical testing: (a1 and b1) The SEM images of the E7 electrode before and after the electrochemical testing, respectively; (a2 and b2) The antimony element distribution maps; (a3 and b3) The oxygen element distribution maps; (a4 and b4) The corresponding EDS spectrum of the mapping area and the insert table was the EDS analysis results; (c1- c3) SEM images at different magnifications after electrochemical testing of pure antimony electrodes; (c4) The corresponding EDS spectrum of E7 electrode surface and the insert table was the EDS analysis results

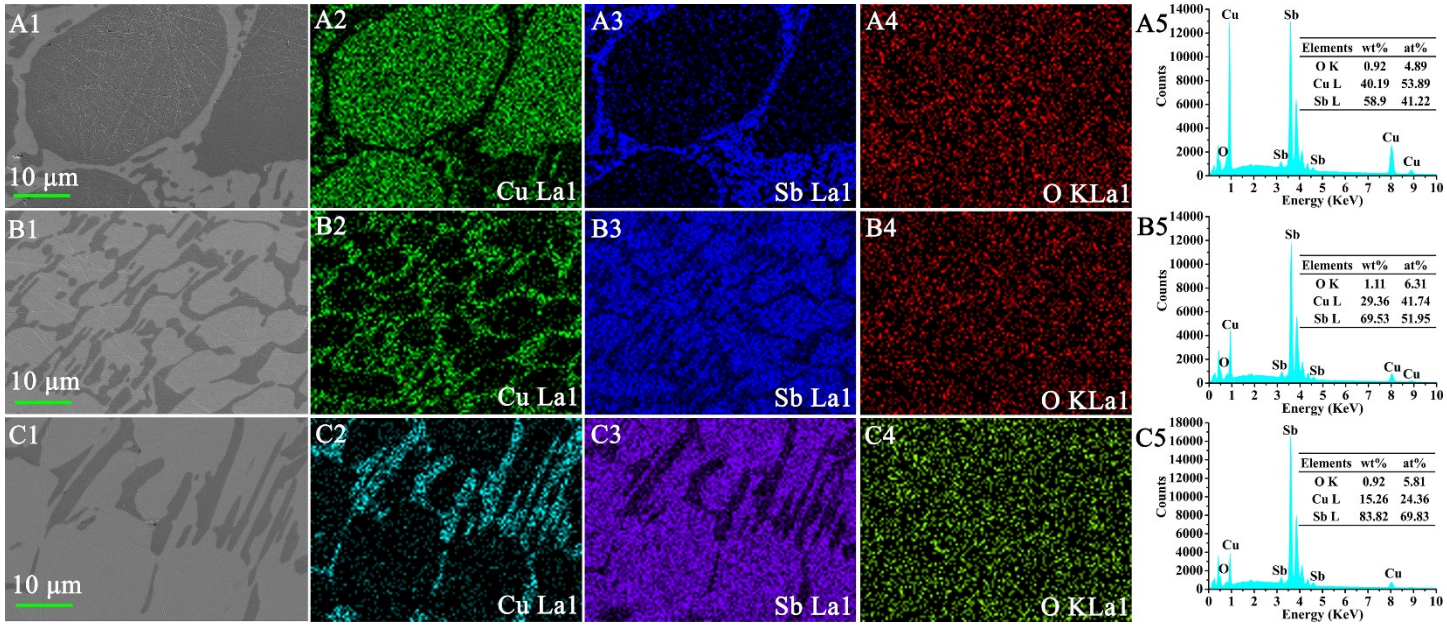


**Figure S12** (A) The SEM images and EDS analysis of the E2，E3 and E6 electrodes surface before the electrochemical testing; (A1, B1, and C1) The SEM images of the E2，E3 and E6 electrodes surface before the electrochemical testing; (A2, B2, and C2) The copper element distribution map of the E2, E3 and E6 electrodes; (A3, B3, and C3) The antimony element distribution map of the E2, E3 and E6 electrodes; (A4, B4, and C4) The oxygen element distribution map of the E2, E3 and E6 electrodes; (A5, B5, and C5) The corresponding EDS spectrum of the mapping area and the insert table was the EDS analysis results of the E2, E3 and E6 electrodes

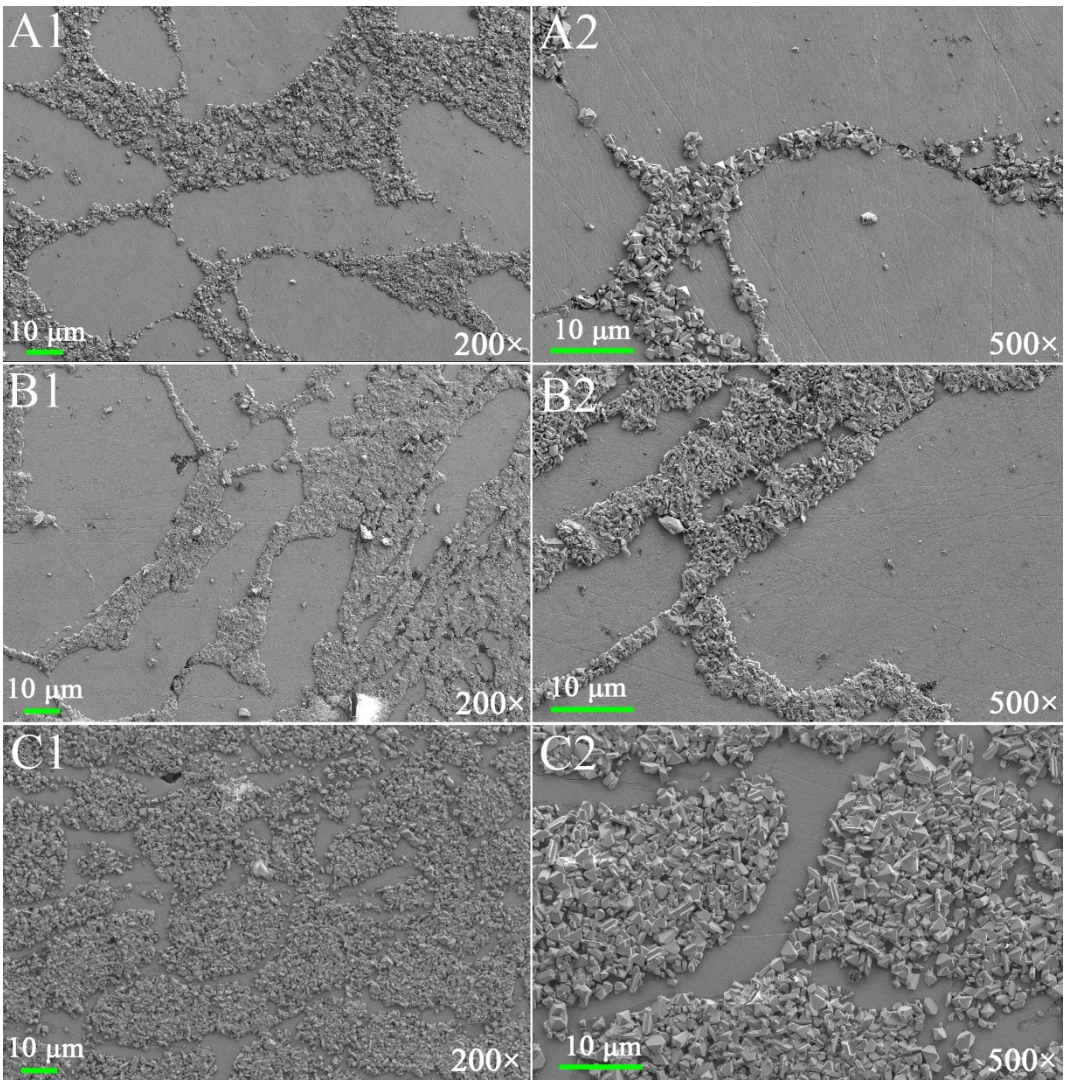


**Figure S13** (A1, A2) SEM images at different magnifications after electrochemical testing of E2 electrode; (B1, B2) SEM images at different magnifications after electrochemical testing of E3 electrode; (C1, C2) SEM images at different magnifications after electrochemical testing of E6 electrode

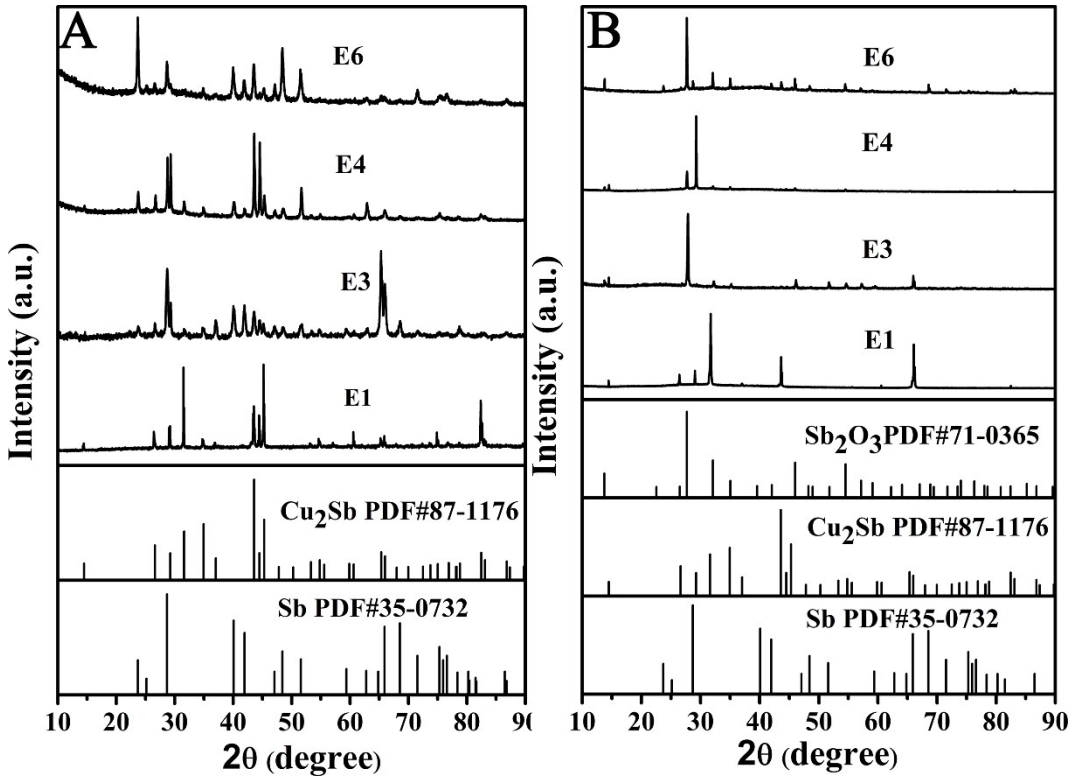


**Figure S14** (A) XRD diffraction patterns of E1, E3, E4, and E6 electrodes before electrochemical testing; (B) XRD diffraction patterns of E1, E3, E4, and E6 electrodes after electrochemical testing

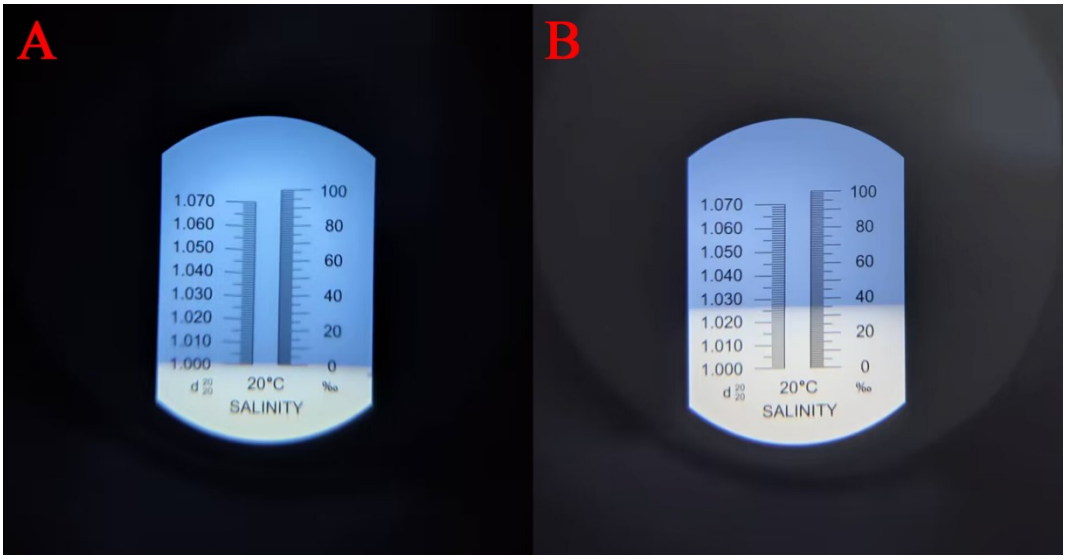


**Figure S15** (A) Zero scale line of salinity meter; (B) The reading of salinity meter for testing seawater salinity

**Table S1** pH measurement results after adding interfering substances to pH=9.18 standard buffer solution

| Electrode | Solution | | | | | |
|---|---|---|---|---|---|---|
| | pH 9.18+$K_2SO_4$ | pH 9.18+$MgSO_4$ | pH 9.18+$CaCl_2$ | pH 9.18+NaCl | pH 9.18+$KNO_3$ | pH 9.18+$Na_2CO_3$ |
| E2 | 9.16±0.08 | 8.89±0.07 | 8.73±0.07 | 8.95±0.07 | 9.13±0.08 | 10.51±0.06 |
| E3 | 9.13±0.05 | 8.78±0.04 | 8.66±0.06 | 8.91±0.04 | 9.08±0.04 | 10.63±0.03 |
| E4 | 9.15±0.04 | 8.74±0.05 | 8.73±0.04 | 9.01±0.02 | 9.14±0.02 | 10.64±0.05 |
| E5 | 9.21±0.04 | 8.75±0.05 | 8.72±0.04 | 8.95±0.02 | 9.11±0.06 | 10.64±0.06 |
| E6 | 9.19±0.06 | 8.69±0.06 | 8.54±0.04 | 8.96±0.02 | 9.08±0.03 | 10.72±0.06 |
| E7 | 9.16±0.07 | 8.67±0.06 | 8.42±0.05 | 8.91±0.03 | 9.04±0.04 | 10.81±0.07 |
| GE | 9.22±0.03 | 8.81±0.04 | 8.67±0.02 | 9.07±0.02 | 9.18±0.03 | 10.58±0.04 |

**Table S2** pH measurement results after adding interfering substances to pH=6.86 standard buffer solution

| Electrode | Solution | | |
|---|---|---|---|
| | pH 6.86+$K_2SO_4$ | pH 6.86+NaCl | pH 6.86+$KNO_3$ |
| E2 | 6.93±0.07 | 6.83±0.06 | 6.91±0.06 |
| E3 | 6.83±0.03 | 6.75±0.05 | 6.85±0.02 |
| E4 | 6.82±0.04 | 6.80±0.03 | 6.85±0.05 |
| E5 | 6.83±0.04 | 6.79±0.04 | 6.81±0.03 |
| E6 | 6.86±0.04 | 6.85±0.06 | 6.87±0.03 |
| E7 | 7.04±0.04 | 6.96±0.05 | 6.97±0.05 |
| Glass Electrode | 6.78±0.03 | 6.68±0.02 | 6.78±0.02 |

**Table S3** pH measurement results after adding interfering substances to pH=4.01 standard buffer solution

| Electrode | Solution | | | | |
|---|---|---|---|---|---|
| | pH 4.01+$K_2SO_4$ | pH 4.01+NaCl | pH 4.01+$KNO_3$ | pH 4.01+$MgSO_4$ | pH 4.01+$CaCl_2$ |
| E2 | 4.50±0.07 | 4.21±0.06 | 4.56±0.06 | 4.17±0.05 | 4.19±0.05 |
| E3 | 4.04±0.03 | 3.78±0.05 | 4.08±0.05 | 3.75±0.04 | 3.67±0.04 |
| E4 | 3.90±0.03 | 3.78±0.04 | 4.06±0.05 | 3.68±0.03 | 3.54±0.03 |
| E5 | 3.96±0.03 | 3.79±0.03 | 4.03±0.03 | 3.74±0.03 | 3.51±0.03 |
| E6 | 3.99±0.04 | 3.78±0.03 | 4.05±0.04 | 3.79±0.03 | 3.56±0.03 |
| E7 | 4.1±0.07 | 3.82±0.05 | 4.08±0.06 | 3.8±0.06 | 3.61±0.04 |
| Glass Electrode | 3.91±0.02 | 3.83±0.02 | 3.99±0.03 | 3.71±0.02 | 3.57±0.02 |

**Table S4** Polarization parameters of the prepared electrodes immersed in the standard buffer solutions of different pH values

| Electrode | pH 4.01 | | | | | pH 6.86 | | | | | pH 9.18 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\beta_{Ano}$ /mV | $\beta_{Cat}$ /mV | $E_{corr}$ /mV | $I_{corr}$ /(A·cm$^{-2}$) | $R_p$ /(Ω·cm$^{-2}$) | $\beta_{Ano}$ /mV | $\beta_{Cat}$ /mV | $E_{corr}$ /mV | $I_{corr}$ /(A·cm$^{-2}$) | $R_p$ /(Ω·cm$^{-2}$) | $\beta_{Ano}$ /mV | $\beta_{Cat}$ /mV | $E_{corr}$ /mV | $I_{corr}$ /(A·cm$^{-2}$) | $R_p$ /(Ω·cm$^{-2}$) |
| E1 | 10.92 | 5.34 | -29 | 3.01-06 | 7924.3 | 11.17 | 1.36 | -58 | 6.1E-06 | 6225.2 | 6.49 | 5.93 | -133 | 5.99E-06 | 5441.9 |
| E2 | 4.43 | 10.14 | -178 | 3.37E-06 | 9912.7 | 3.38 | 4.80 | -306 | 4.76E-06 | 7468.8 | 5.21 | 3.77 | -445 | 7.16E-06 | 6761.5 |
| E3 | 5.54 | 4.03 | -200 | 4.99E-06 | 9097.4 | 4.89 | 4.54 | -342 | 5.34E-06 | 6515.5 | 4.97 | 3.16 | -449 | 1.06E-05 | 5043.2 |
| E4 | 5.40 | 4.55 | -201 | 5.07E-06 | 8617.6 | 4.95 | 4.08 | -347 | 6.66E-06 | 5901.6 | 4.95 | 3.28 | -446 | 1.18E-05 | 4462.0 |
| E5 | 6.21 | 2.95 | -203 | 6.12E-06 | 7756.5 | 4.77 | 3.79 | -349 | 8.21E-06 | 5758.2 | 5.02 | 2.76 | -446 | 1.19E-05 | 4628.1 |
| E6 | 7.12 | 2.16 | -210 | 6.29E-06 | 7472.5 | 5.78 | 3.03 | -359 | 1.09E-05 | 4623.8 | 4.99 | 3.35 | -453 | 1.23E-05 | 4215.7 |
| E7 | 7.10 | 3.50 | -219 | 9.68E-06 | 4239.1 | 6.24 | 2.44 | -369 | 1.52E-05 | 3284.0 | 4.63 | 3.32 | -457 | 1.53E-05 | 3583.3 |

**Table S5** Compositions of the buffer with addition of 0.59 mol·L$^{-1}$ NaCl

| | Composition (mol L$^{-1}$) | | | pH |
|---|---|---|---|---|
| | $KH_2PO_4$ | NaOH | NaCl | |
| Buffer 1 | 0.1000 | | 0.59 | 4.31 |
| Buffer 2 | 0.0900 | 0.0074 | 0.59 | 5.33 |
| Buffer 3 | 0.0630 | 0.0350 | 0.59 | 6.41 |
| Buffer 4 | 0.0519 | 0.0478 | 0.59 | 7.11 |
| | $NaHCO_3$ | NaOH | NaCl | |
| Buffer 5 | 0.0455 | 0.0091 | 0.59 | 9.00 |
| Buffer 6 | 0.0363 | 0.0335 | 0.59 | 10.31 |

**Table S6** Comparison of the pH electrode in this work with other pH electrodes reported

| Electrode types | Sensitivity (mV/pH) | pH range | Response time (s) | Stability | Hysteresis (mV) | Method | References |
|---|---|---|---|---|---|---|---|
| Sb nanowires | 55.9 | 2-10 | 10 | - | - | focused ion beam based approach | [1] |
| Sb film | 74.0 | 4-9 | < 3 | < 2 mV in 700 s | - | magnetron sputtering and heat treated | [2] |
| Sb film | 67.3 | 4-9 | < 3.5 | < 2 mV in 700 s | <1.3 | magnetron sputtering and thermal annealing | [3] |
| Sb film | 62.57 | 4-9 | 7.1 | 1.60 mV $h^{-1}$ | 1.58 | magnetron sputtering | [4] |
| $TiO_2$-Sb-$SbO_x$ films | 68 ± 6 | 2-10 | - | - | - | plasma electrolytic oxidation | [5] |
| Mg-doped $Sb_2O_3$ membrane | 60.17 | 2-12 | - | 1.99 mV $h^{-1}$ | 4.29 | Sputtering and rapid thermal annealing | [6] |
| Ir-$IrO_X$ | -56± 1 | 2-10 | 1 | < 0.65 mV in 48 h | - | Carbonate-melt oxidation | [7] |
| $IrO_2$ membrane | -74.45 | 2-12 | | Acidity 0.14 mV $h^{-1}$ Neutral -0.76 mV $h^{-1}$ Alkalinity 57.75 mV $h^{-1}$ | 4.21-16.97 | Electrodeposition | [8] |
| $RuO_2$ | -55.3 | 2-6 | 55 ± 23 | 7.2 mV $h^{-1}$ | <1 | Laser-etched sputter deposited | [9] |
| $RuO_2$−CuO | 54.3 ± 6.4 | 3-11 | - | 5 mV $h^{-1}$ | 5 ± 2 | Screen printing | [10] |
| PdO thin film | -62.87 | 2-12 | | 2.32 mV $h^{-1}$ | 7.9 | Reactive electron beam evaporation | [11] |
| Pd/ PdO films | 64.71± 0.56 | 2-12 | < 18 | 3.25 mV $h^{-1}$ | < 8 | Solution processing | [12] |
| Cu-Sb alloy rod | -54.38 | 2-12 | 1 | 0.07-0.12 mV $h^{-1}$ | <3 | Melt casting method | This work |

## Reference


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