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

Supplementary Information

Regulating solvation and interface chemistry to inhibit corrosion of aluminum anode in aluminum-air batteries

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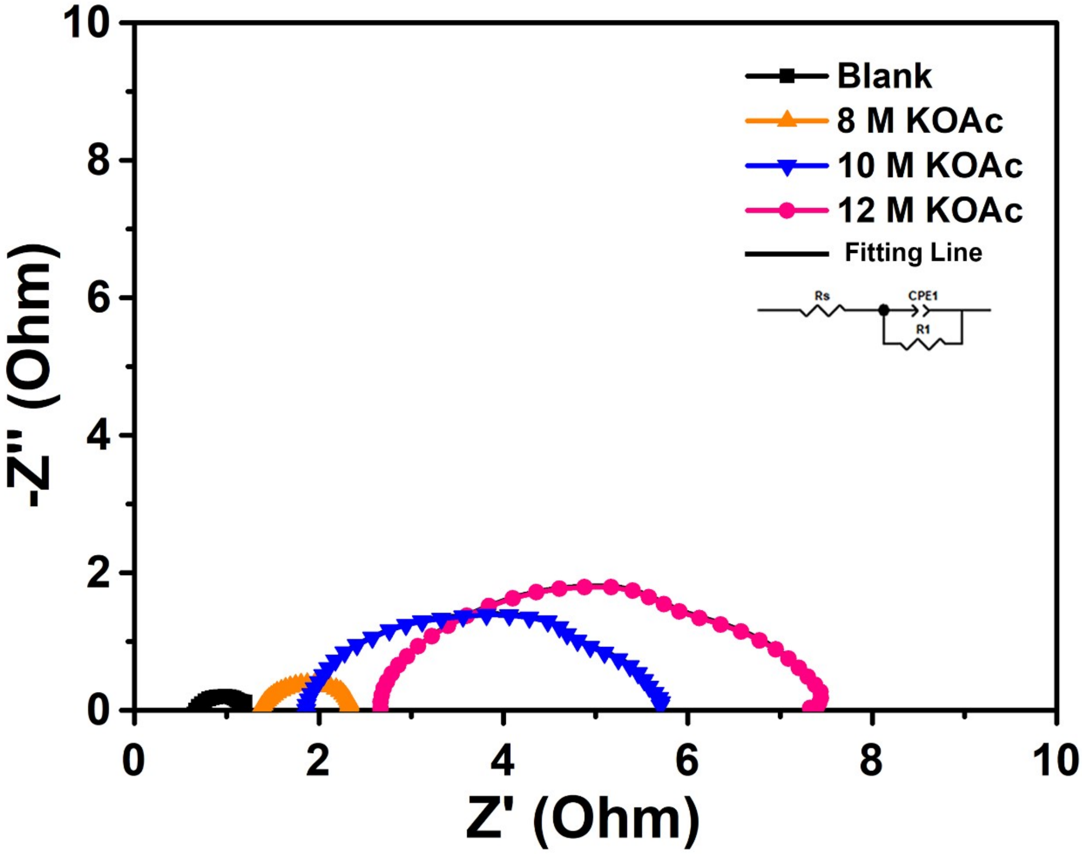

Fig. S1. Electrochemical independence spectra (EIS) of 4 M KOH solution with different KOAc.

As shown in Fig. S1, both the internal resistance and charge-transfer resistance of the electrolyte are significantly increased when 10 M KOAc was added to 4 M KOH, which increase the polarization of battery. In addition, corrosion rate is gradually decreases with the addition of Na_2SnO_3, and the lowest corrosion rate of 0.011 mg cm^{-2} min^{-1} is noted in the 4 M KOH solution containing 8 M KOAc + 0.02 M Na_2SnO_3 (Table S2). Taking into account the battery polarization and corrosion rate, we choose the 8 M KOAc + 0.02 M Na_2SnO_3 as optimal electrolyte.

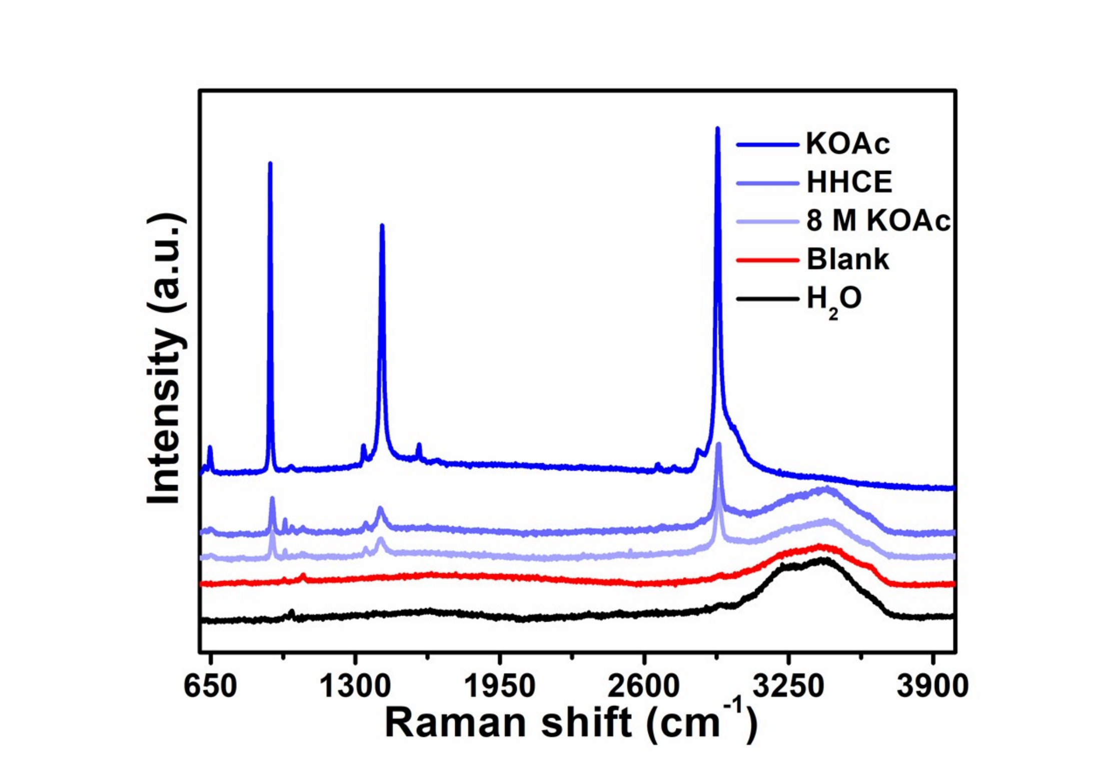

Fig. S2. Raman spectra of different electrolytes (KOAc crystal and H_2O as reference)

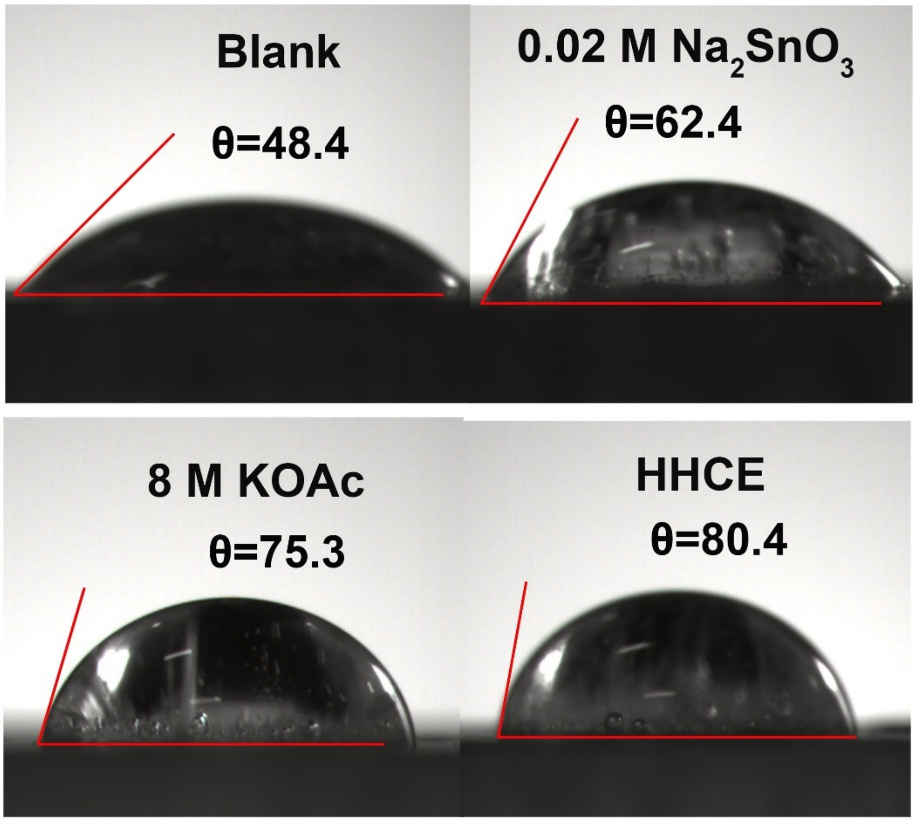

Fig. S3. The contact angel images of different electrolytes.

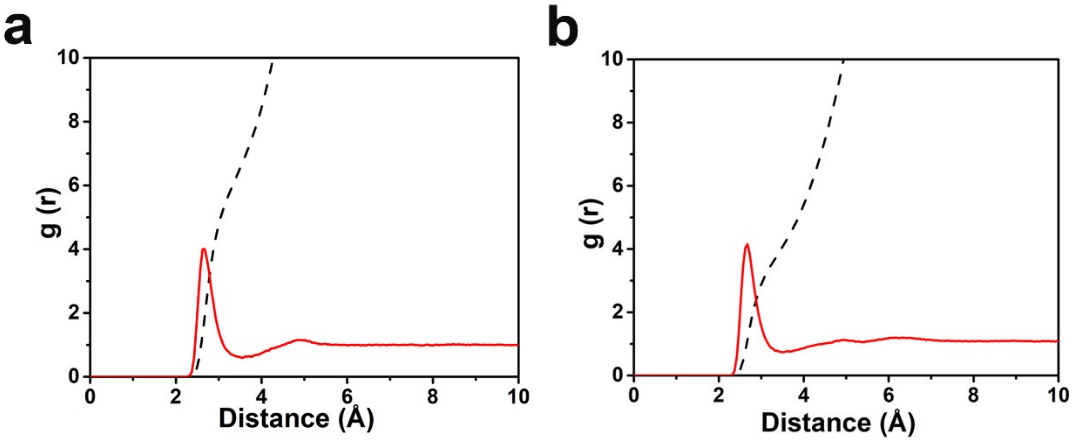

Fig. S4. Radial distribution functions (solid line) and integral curves (dashed line) of KOH electrolyte (a) and 8 M KOAc electrolyte (b).

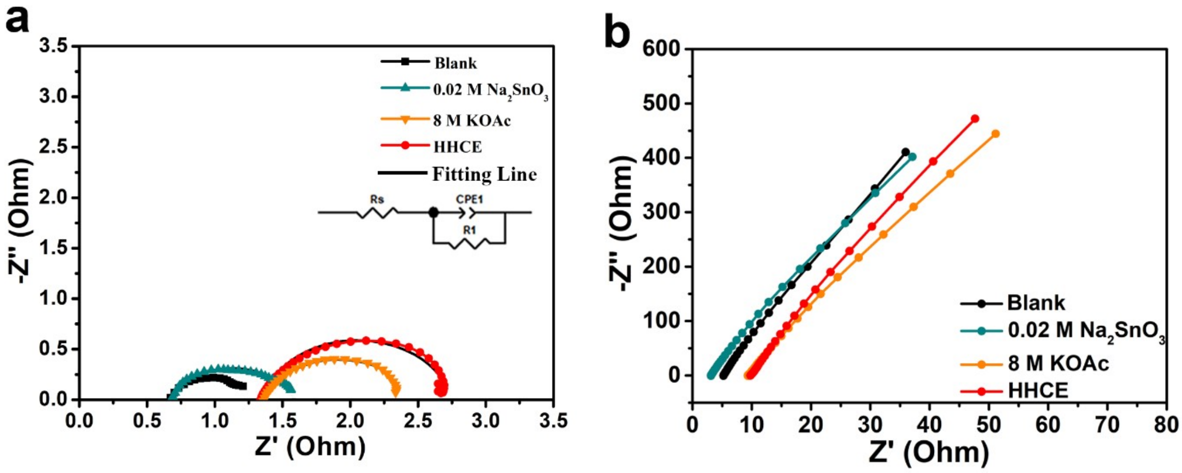

Fig. S5. EIS under three electrode condition (aluminum alloy as working electrode, Pt as counter electrode and Hg/HgO as reference electrode) (a) and two stainless steel condition (b), respectively.

The larger viscosity of HHCE hindered ion diffusion, which is the main reason for higher resistance. It can be found that the charge transfer resistance is increased by comparing the HHCE and 8 M KOAc, 0.02 M Na_2SnO_3 and blank, which can be explained that the tight protective layer on aluminum anode surface. Although the Sn layer mitigate interface electron migration rate, it significantly inhibits the self-corrosion of aluminum anode.

The related EIS parameters have shown below (Table S3). R_s represents the internal resistance of electrolyte, CPE is constant phase-angle elements, R_1 is corresponding to the charge-transfer resistance, respectively. It is obvious that the semicircle diameters (R_1) increase with add of the 0.02 M Na_2SnO_3 in blank solution. It indicates that additives molecules are adsorbed on the electrode surface to form a protective layer and led to an increase in the charge transfer resistance, thus decreasing the corrosion rate.

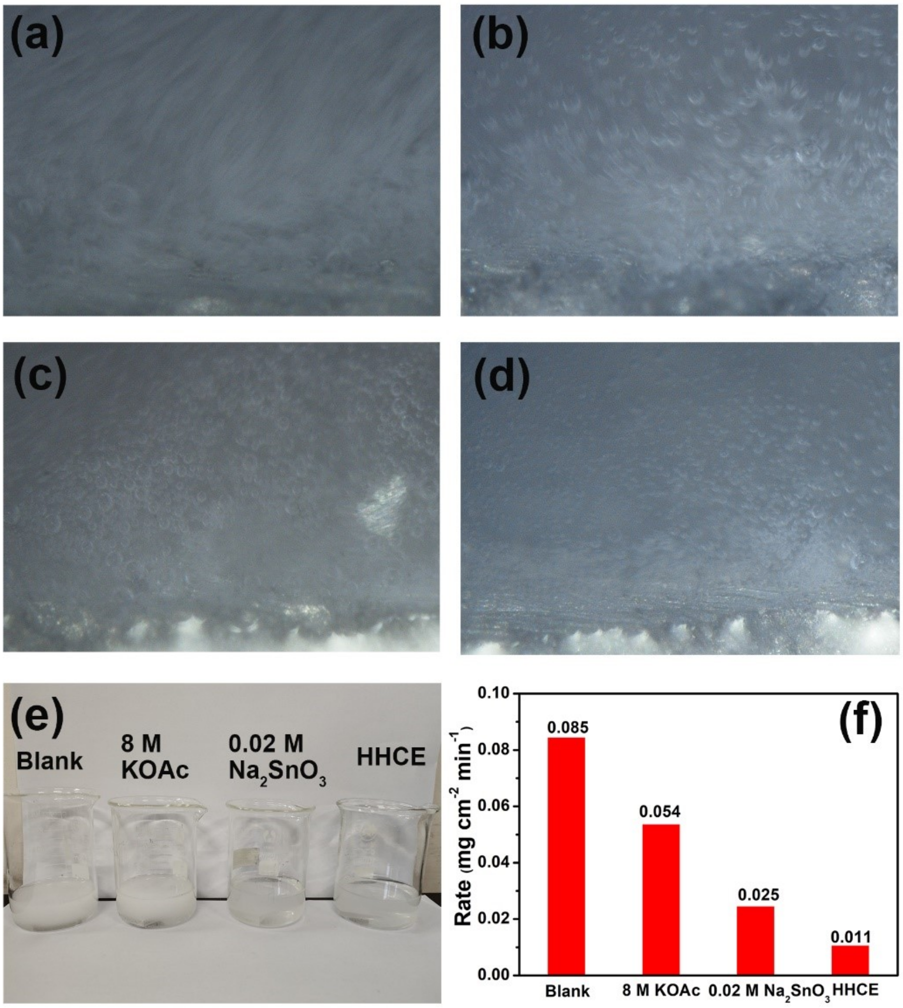

Fig. S6. In-situ optical microscope images of aluminum anode surface in different electrolytes: (a) blank, (b) 8 M KOAc, (c) 0.02 M Na_2SnO_3 and (d) HHCE. (e) Optical microscope image of aluminum anode in different electrolytes. (f) Aluminum anode corrosion rate.

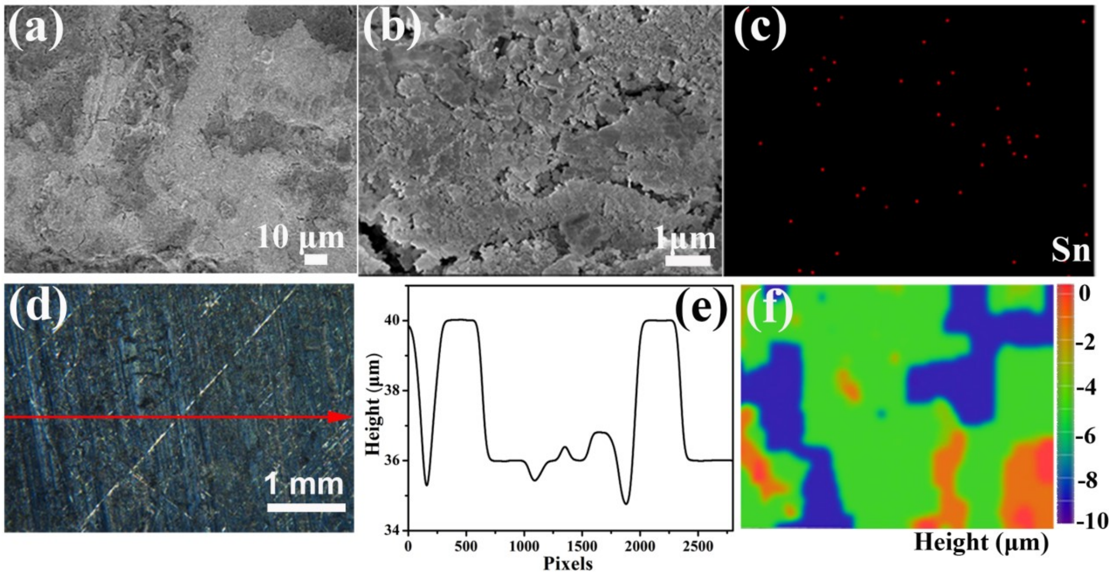

Fig. S7. SEM-EDS (a)-(c), and in-situ optical microscope images of aluminum anode surface (d)-(f).

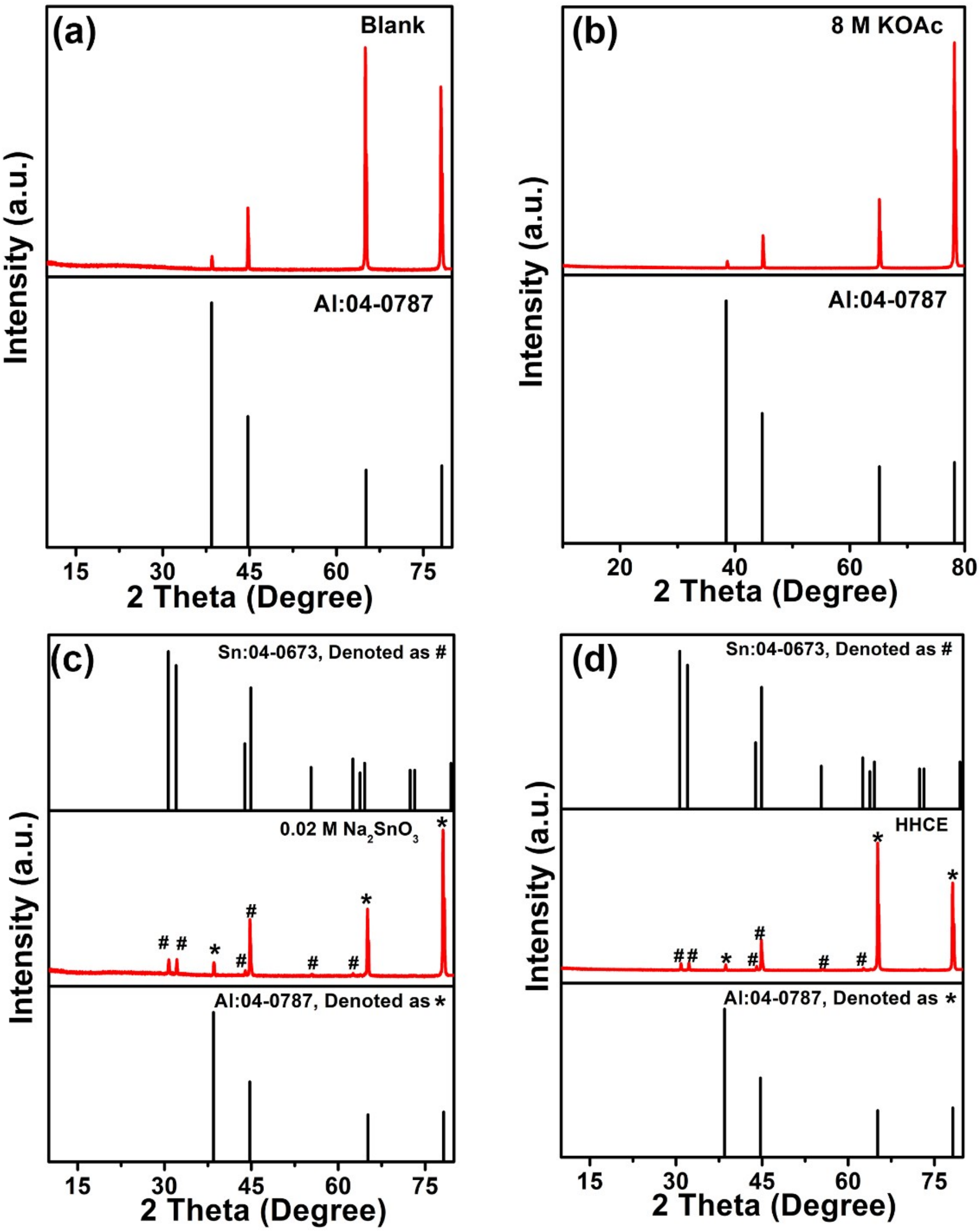

Fig. S8. XRD pattern of aluminum anode surface in (a) blank electrolyte, (b) 8 M KOAc, (c) 0.02 M Na_2SnO_3 and (d) HHCE after immersing for 3 h.

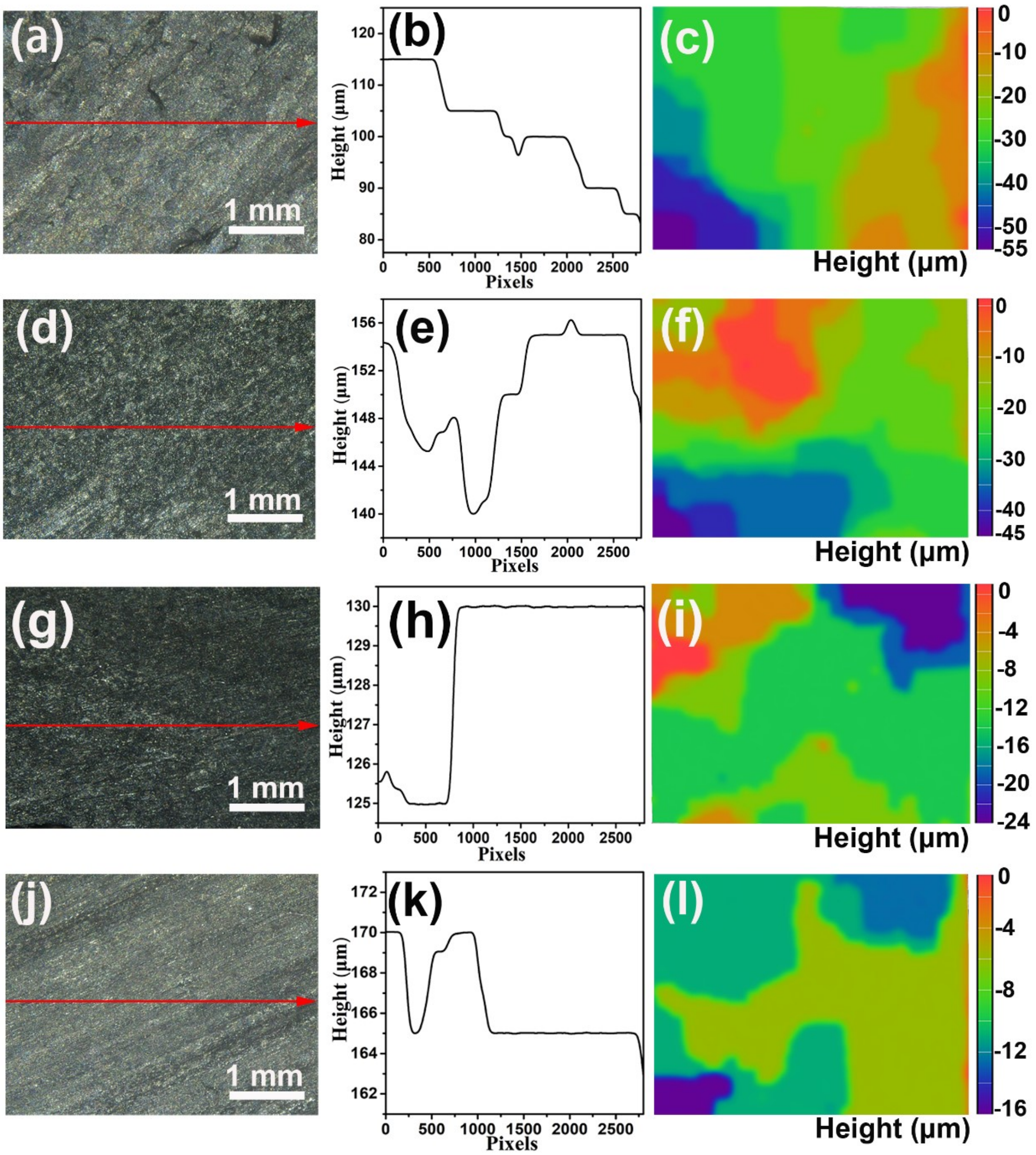

Fig. S9. In-situ optical microscope images of aluminum anode surface in the electrolyte of blank (a)-(c), 8 M KOAc (d)-(f), 0.02 M Na_2SnO_3 (g)-(i), and HHCE (j)-(l) after immersing for 3 h.

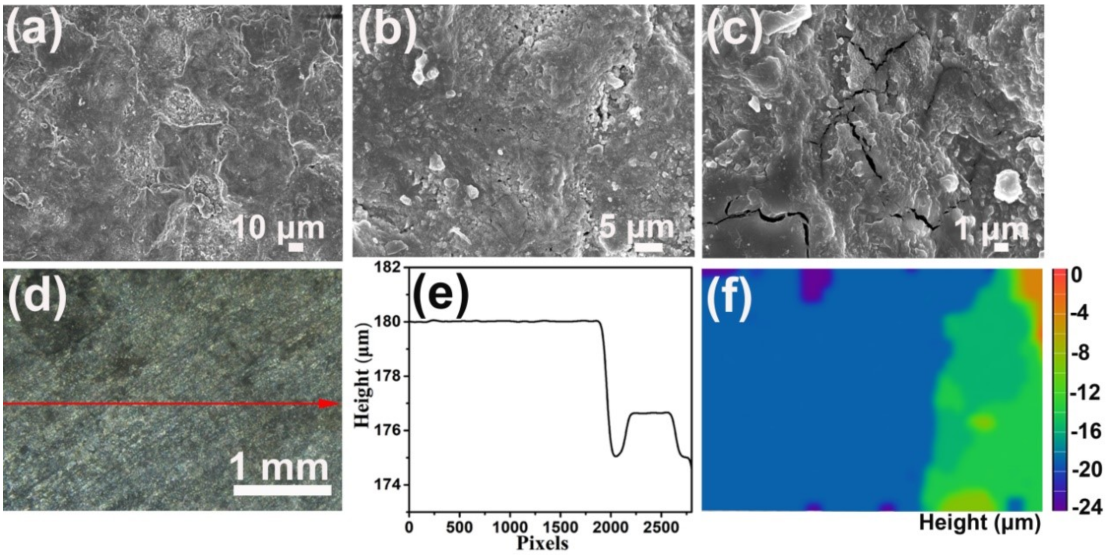

Fig. S10. SEM and in-situ optical microscope images of aluminum anode surface in the electrolyte of 0.02 M Na_2SnO_3 after galvanostatic discharge for 3 h.`

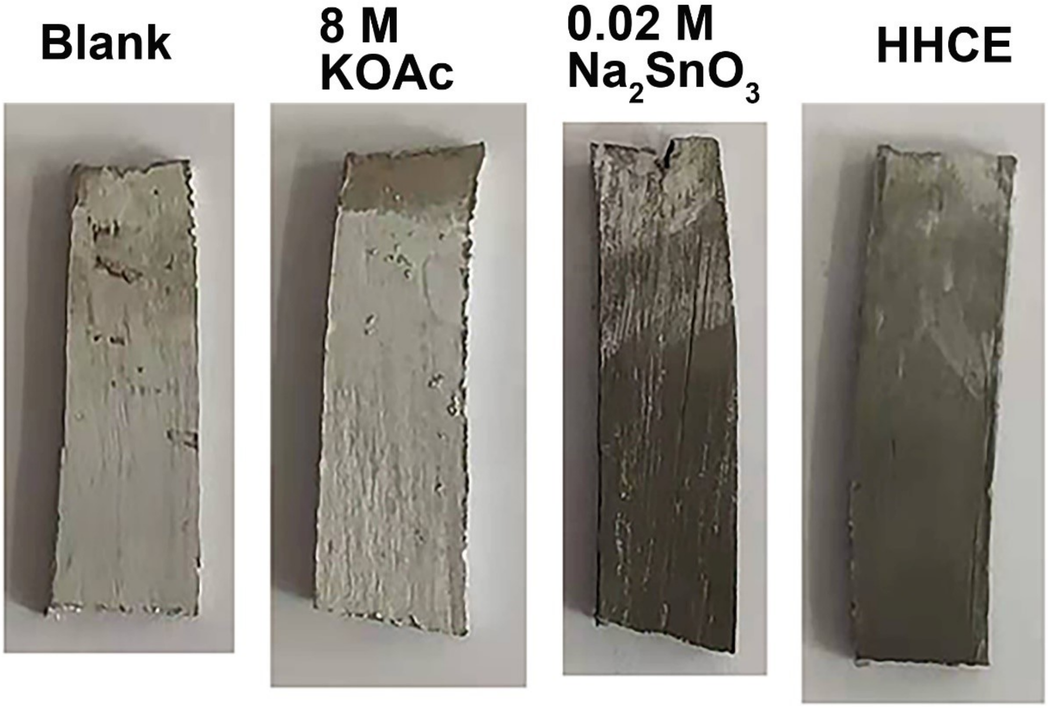

Fig. S11. Optical microscope images of aluminum anode surface in different electrolytes after galvanostatic discharge for 3 h.

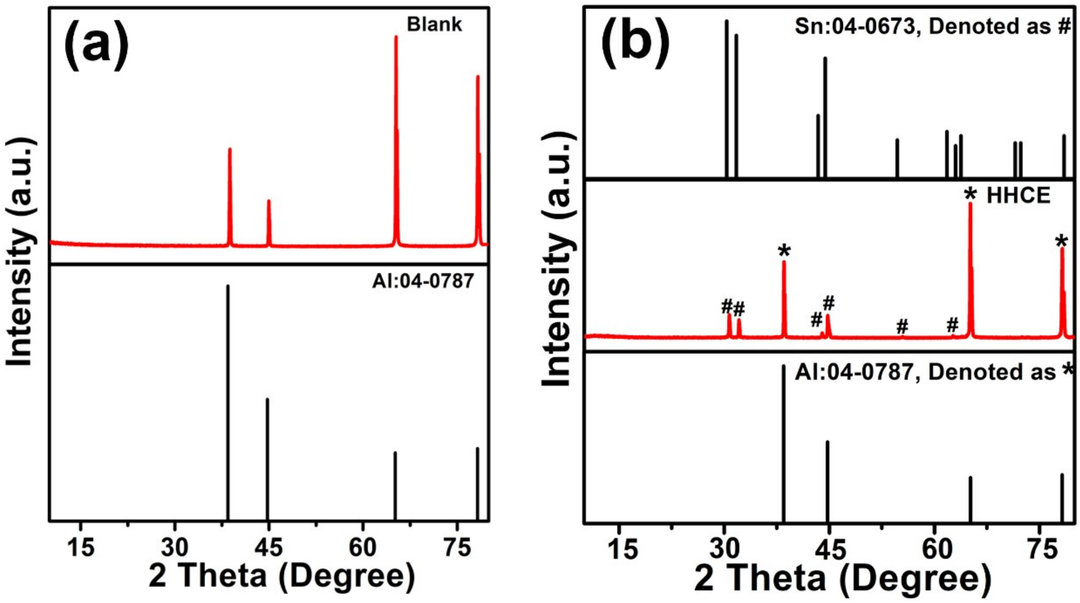

Fig. S12. XRD pattern of aluminum anode surface in (a) blank electrolyte and (b) HHCE after galvanostatic discharge for 3 h.

The change in the intensity ratio of diffraction peaks is due to the different crystal orientations exhibits disparate electrochemical activities and corrosion behavior, which is attributed to the potential differences for each crystalline orientation.[1,2]

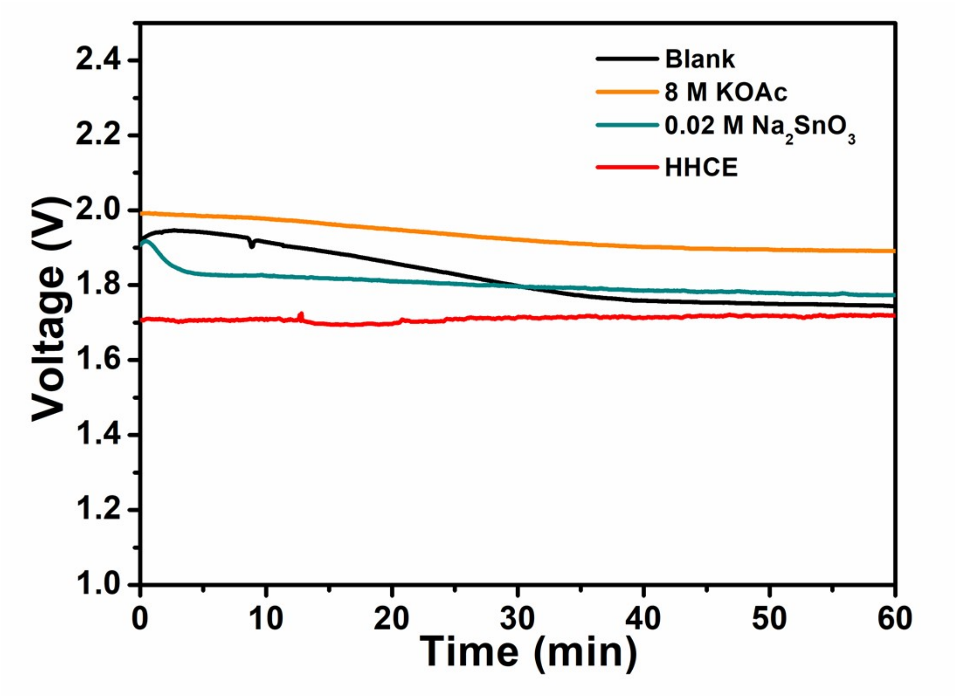

Fig. S13. Open circuit voltage curves of aluminum-air full batteries with different electrolytes.

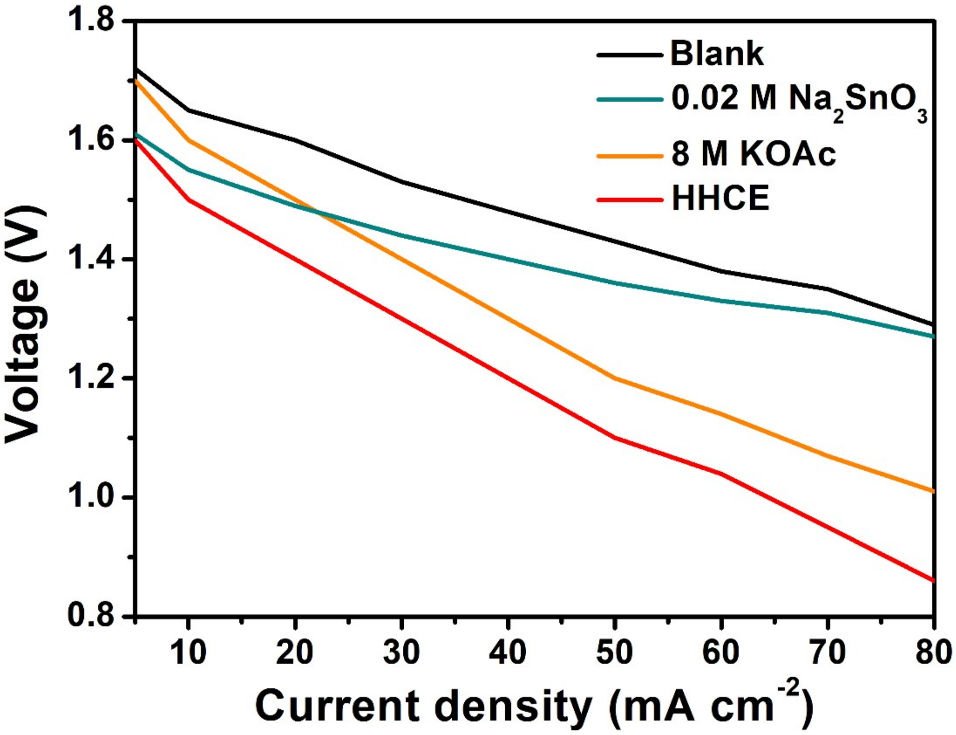

Fig. S14. Discharge polarization curves of aluminum-air full batteries with different electrolytes.

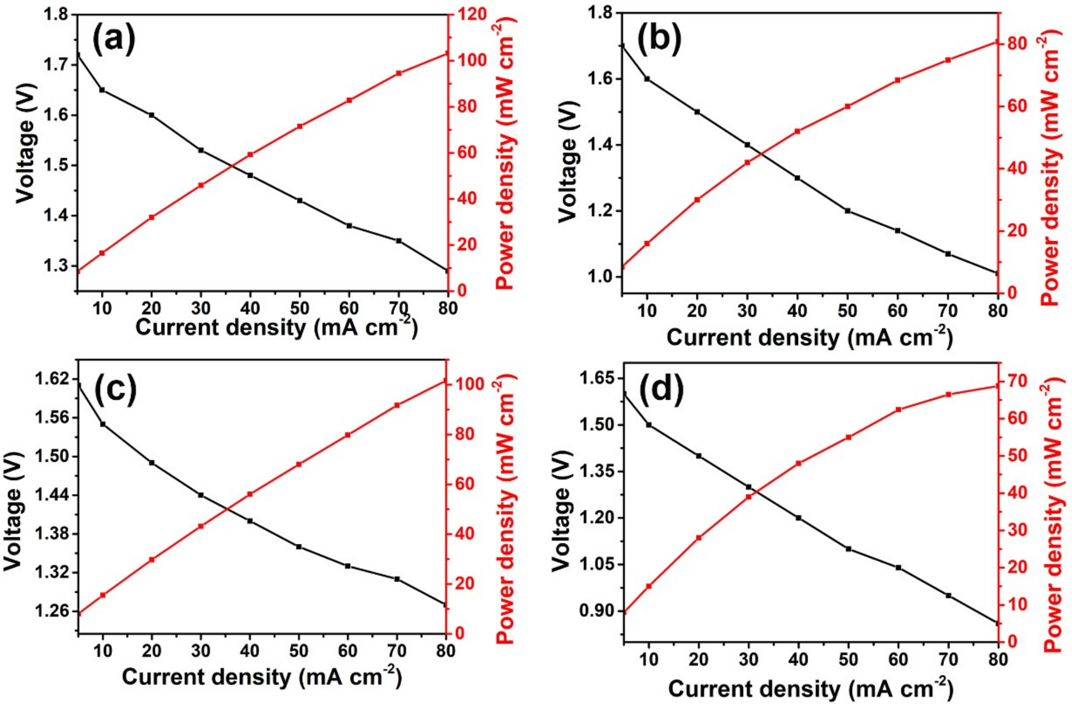

Fig. S15. Voltage and power density versus current density of the constructed aluminum-air batteries in different electrolytes. (a) 4 M KOH, (b) 8 M KOAc, (c) 0.02 M Na_2SnO_3 and (d) HHCE.

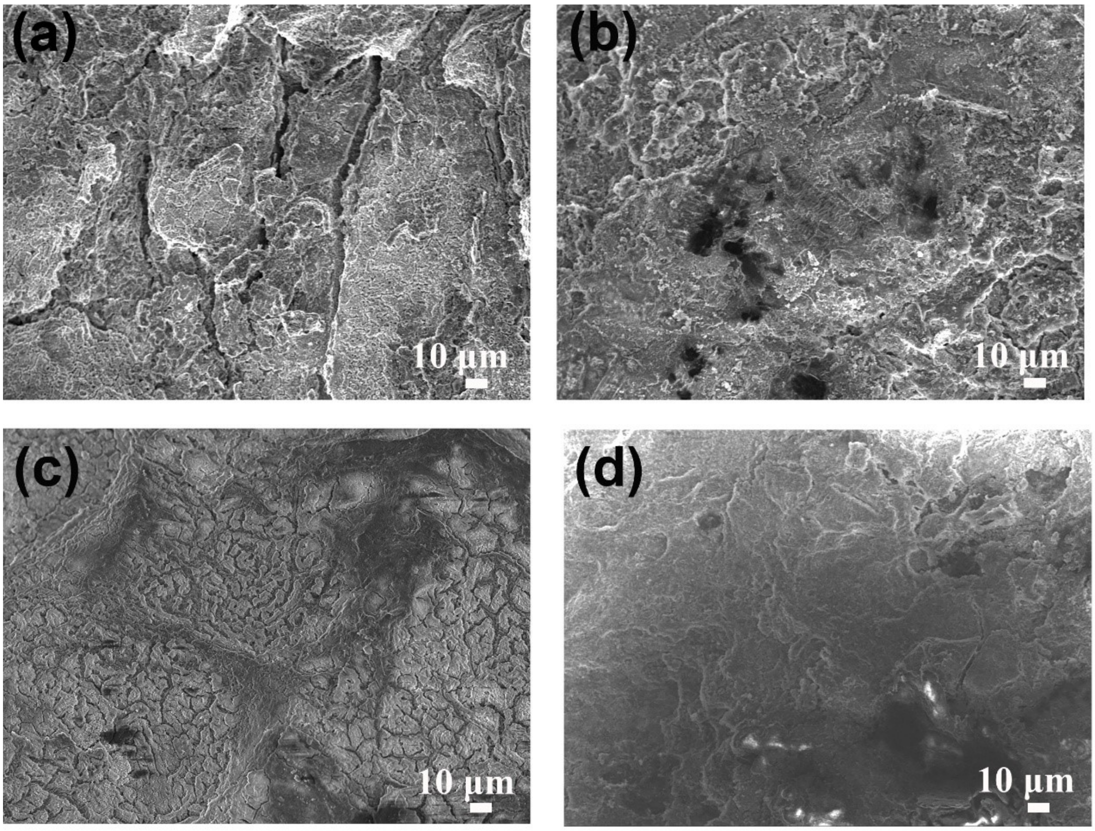

Fig. S16. SEM images of aluminum anode surface in (a) blank electrolyte, (b) 8 M KOAc, (c) 0.02 M Na_2SnO_3 and (d) HHCE after galvanostatic discharge.

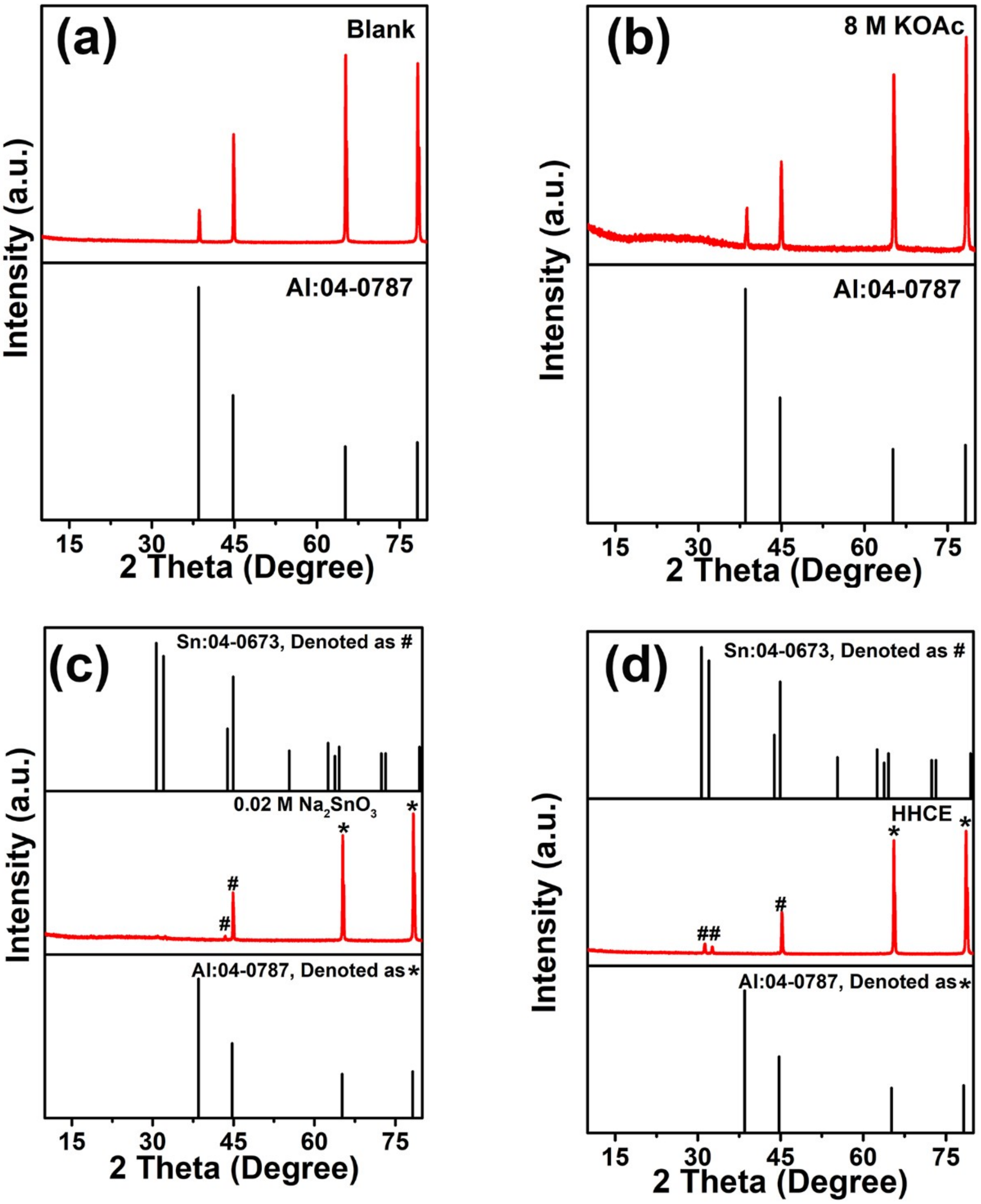

Fig. S17. XRD pattern of aluminum anode surface in (a) blank electrolyte, (b) 8 M KOAc, (c) 0.02 M Na_2SnO_3 and (d) HHCE after galvanostatic discharge.

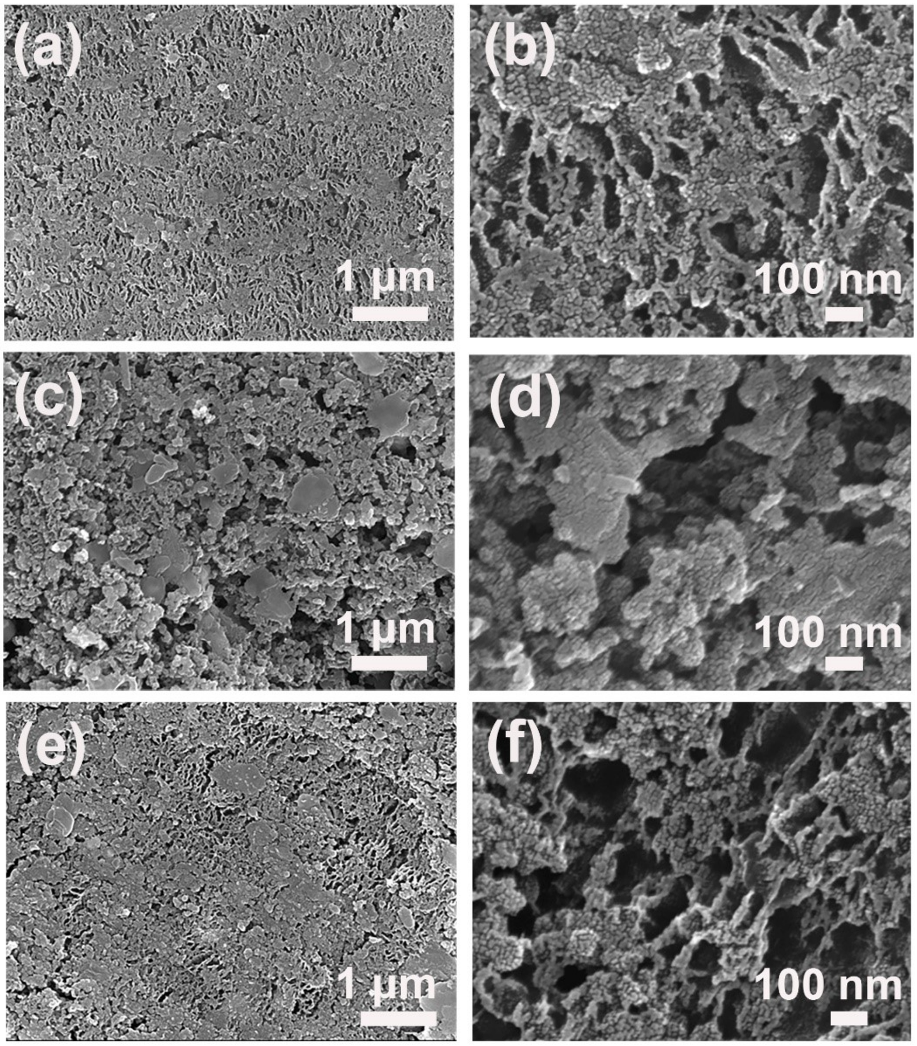

Fig. S18. SEM images of electrocatalyst. (a)-(b) pristine electrocatalyst material, (c)-(d) electrocatalyst after galvanostatic discharge in blank, (e)-(f) electrocatalyst after galvanostatic discharge in HHCE.

Table S1 Chemical compositions of Al alloy (wt %).

Mg	Ga	Sn	Zn	Fe	Cu	Si	Al
0.024	0.011	0.010	0.004	≤0.009	≤0.001	≤0.001	Remainder

Table S2 Corrosion rate of aluminum anode in different electrolyte.

Solution	△m (mg)	R (mg cm^{-2} min^{-1})	η%
Blank	158.2	0.085	-
8 M KOAc	100.6	0.054	36.47
0.02 M Na_2SnO_3	46.1	0.025	70.59
8 M KOAc+0.005 Na_2SnO_3	67.4	0.036	57.64
8 M KOAc+0.01 Na_2SnO_3	39.3	0.021	75.29
8 M KOAc+0.015 Na_2SnO_3	31.8	0.017	80
HHCE	20.1	0.011	87.06
8 M KOAc+0.03 Na_2SnO_3	41.2	0.022	74.11

Table S3 Fitting results of the Nyquist plots using the equivalent circuit.

Electrolyte	R_s (Ω cm^{-2})	CPE		R_1 (Ω cm^{-2})
		Y_0 (Ss^n cm^{-2})	n	
Blank	0.797	9.0×10^{-5}	0.9	0.515
8 M KOAc	1.364	3.1×10^{-4}	0.919	0.966
0.02 M Na_2SnO_3	0.672	9.0×10^{-4}	0.76	0.919
HHCE	1.435	4.0×10^{-4}	0.901	1.379

Table S4 Physicochemical properties of the solutions at 25°C.

Solution	Viscosity [mPa.s]
4 M KOH	1.74
4 M KOH+0.02 M Na_2SnO_3	1.74
4 M KOH+6 M KOAC	3.99
4 M KOH+8 M KOAC	5.43
4 M KOH+8 M KOAC+0.02 M Na_2SnO_3	5.49
4 M KOH+10 M KOAC	6.84

Table S5 Aluminum anode utilization in different electrolyte after galvanostatic discharge for 3 h

Solution	$\triangle$m (mg)	U_a (%)
Blank	0.1545	36.2
8 M KOAc	0.1415	39.6
0.02 M Na_2SnO_3	0.0892	62.7
HHCE	0.0746	75.0

References

1 G.-L. Song and Z. Q. Xu, *Corros. Mater.*, 2012, **63**, 100-112.

2 G.-L. Song, R. Mishra and Z. Q. Xu, *Electrochem. Commun.*, 2010, **12,** 1009-1012.