

Engineering the Hydrogen Evolution Reaction of Transition Metals: Effect of Li Ions

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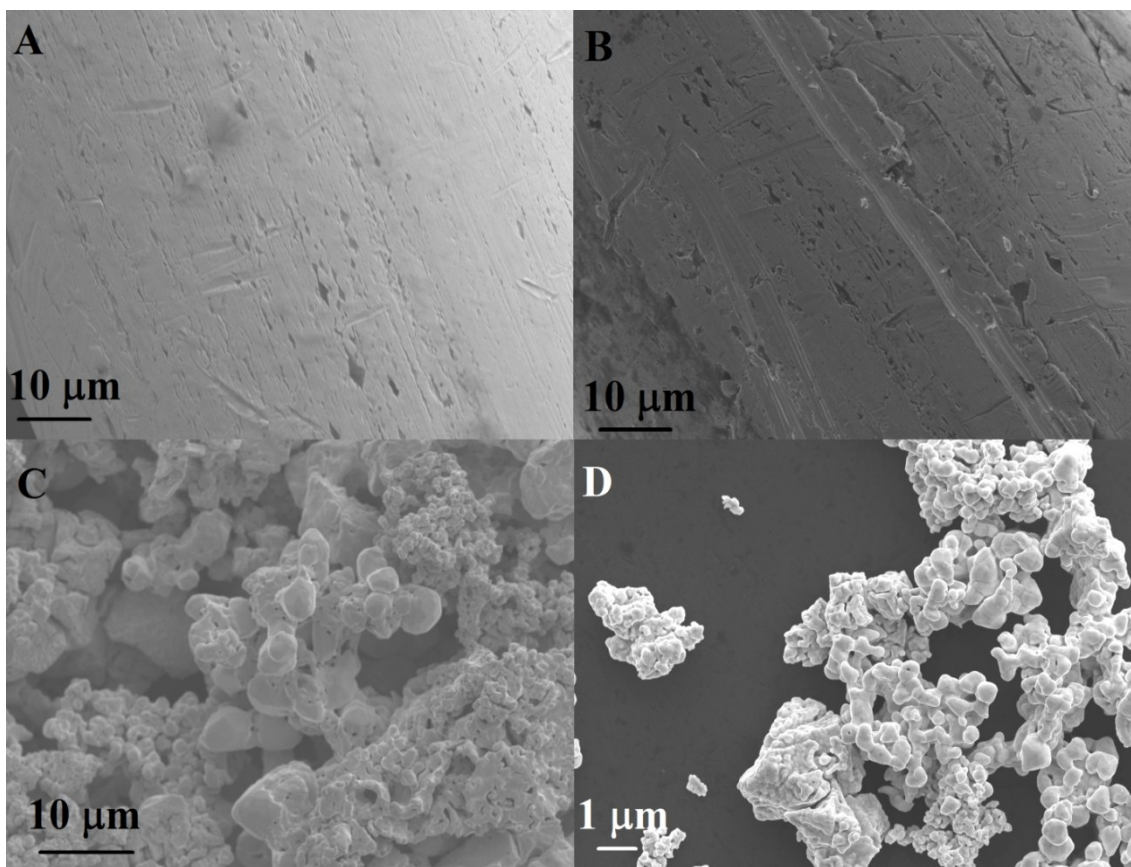


Figure S1: SEM images of (A) Pt, (C) Ir before and, (B) Pt, (D) Ir after electro-cycled in 20M LiTFSI.

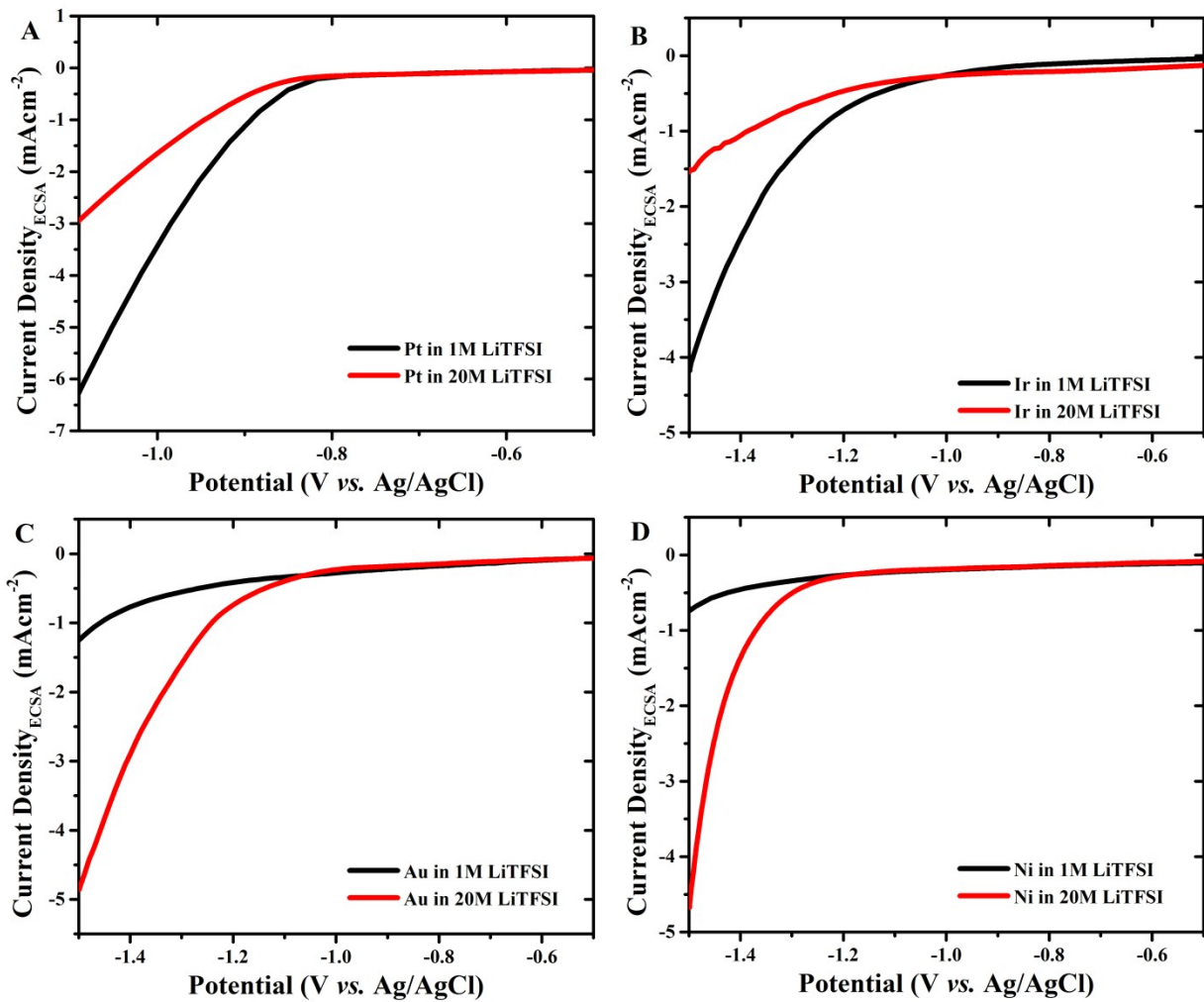


Figure S2: LSVs of (A) Pt, (B) Ir, (C) Au and, (D) Ni in 1M and 20 M LiTFSI with respect to electrochemically active surface area (ECSA). Scan rate 50 mV/s.

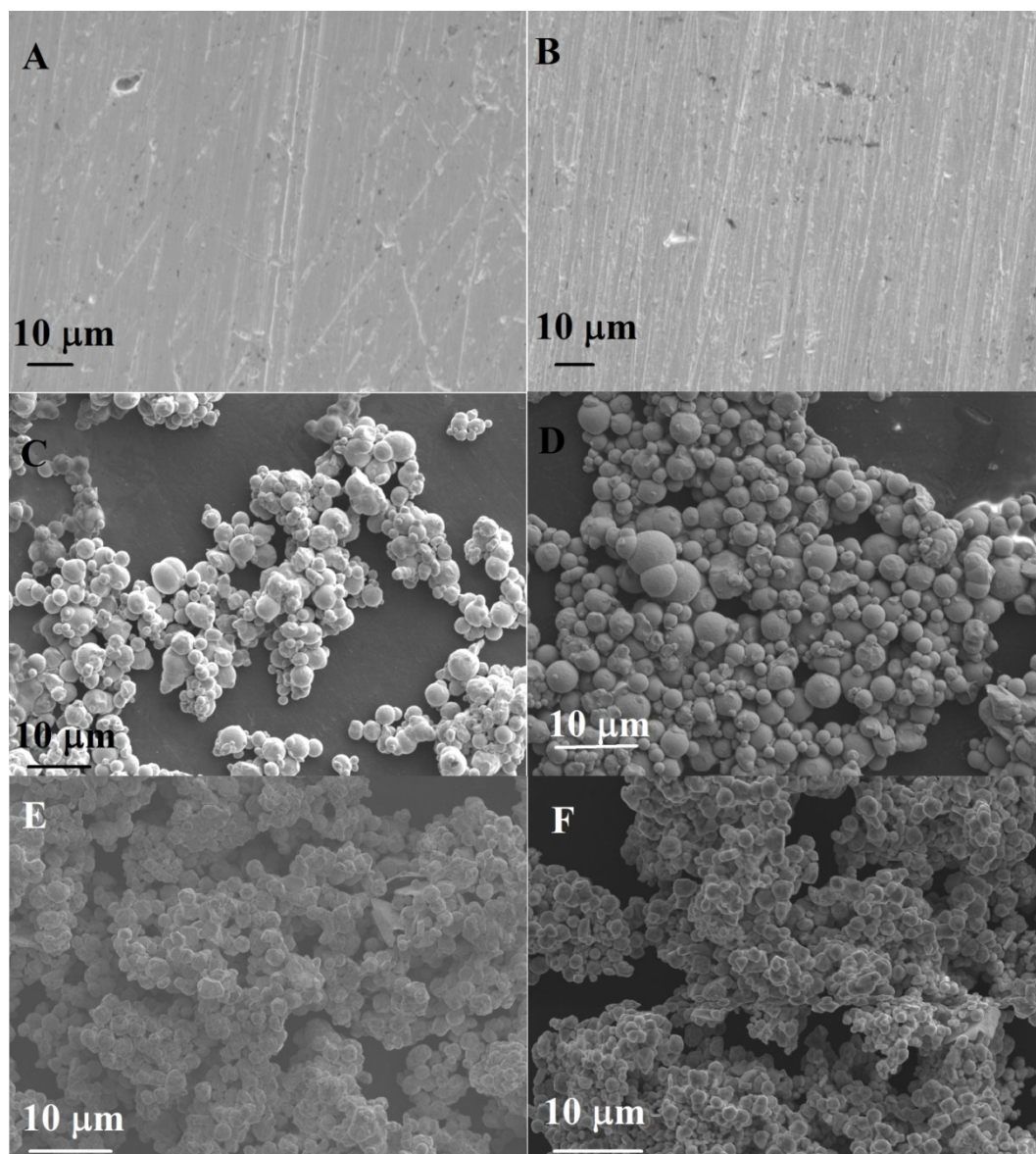


Figure S3: SEM images of (A) Au, (C) Fe, (E) Ni before and, (B) Au, (D) Fe, (F) after electrocycled in 20M LiTFSI.

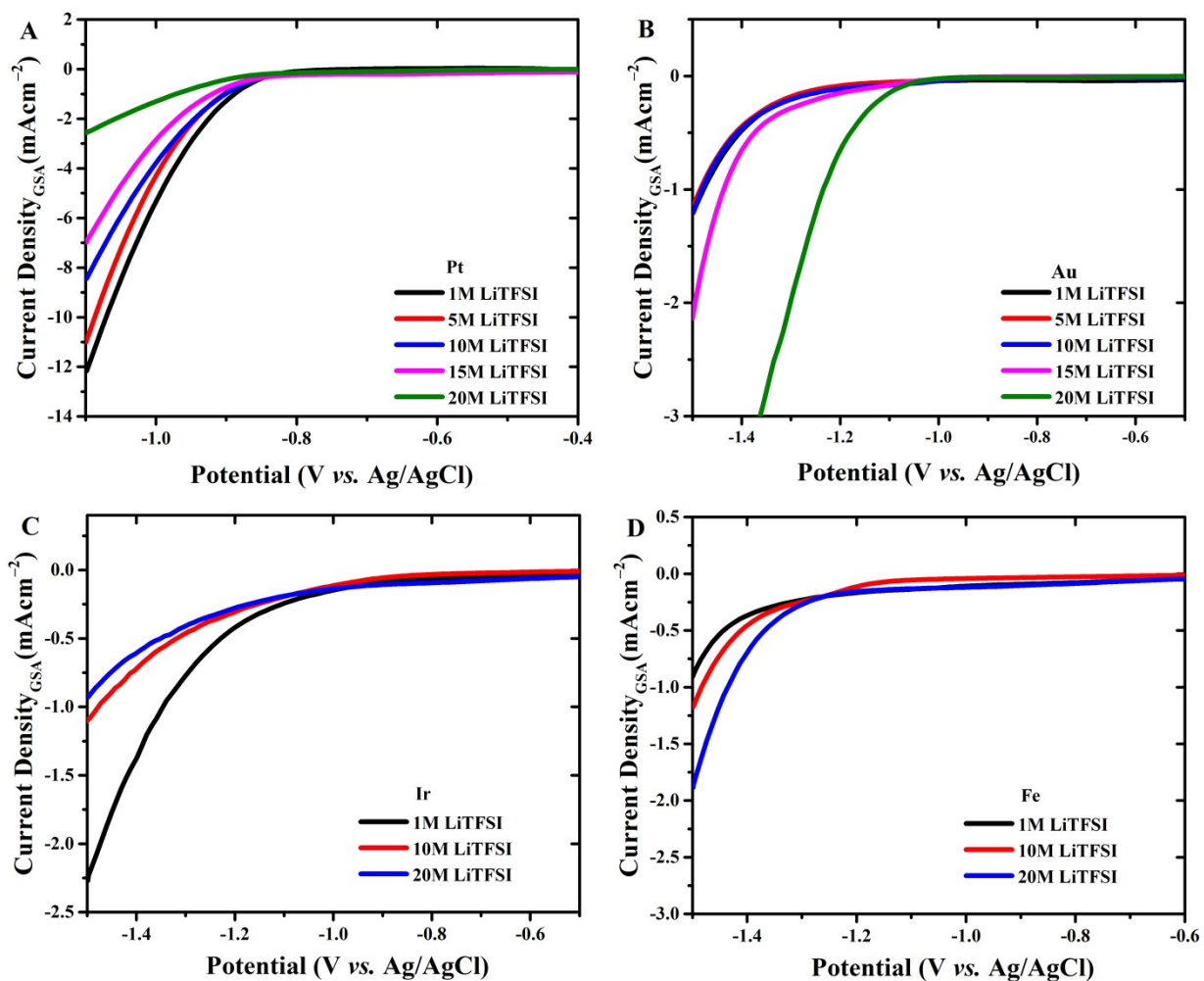


Figure S4: LSVs of (A) Pt, (B) Au, (C) Ir and, (D) Fe in varying LiTFSI concentration.

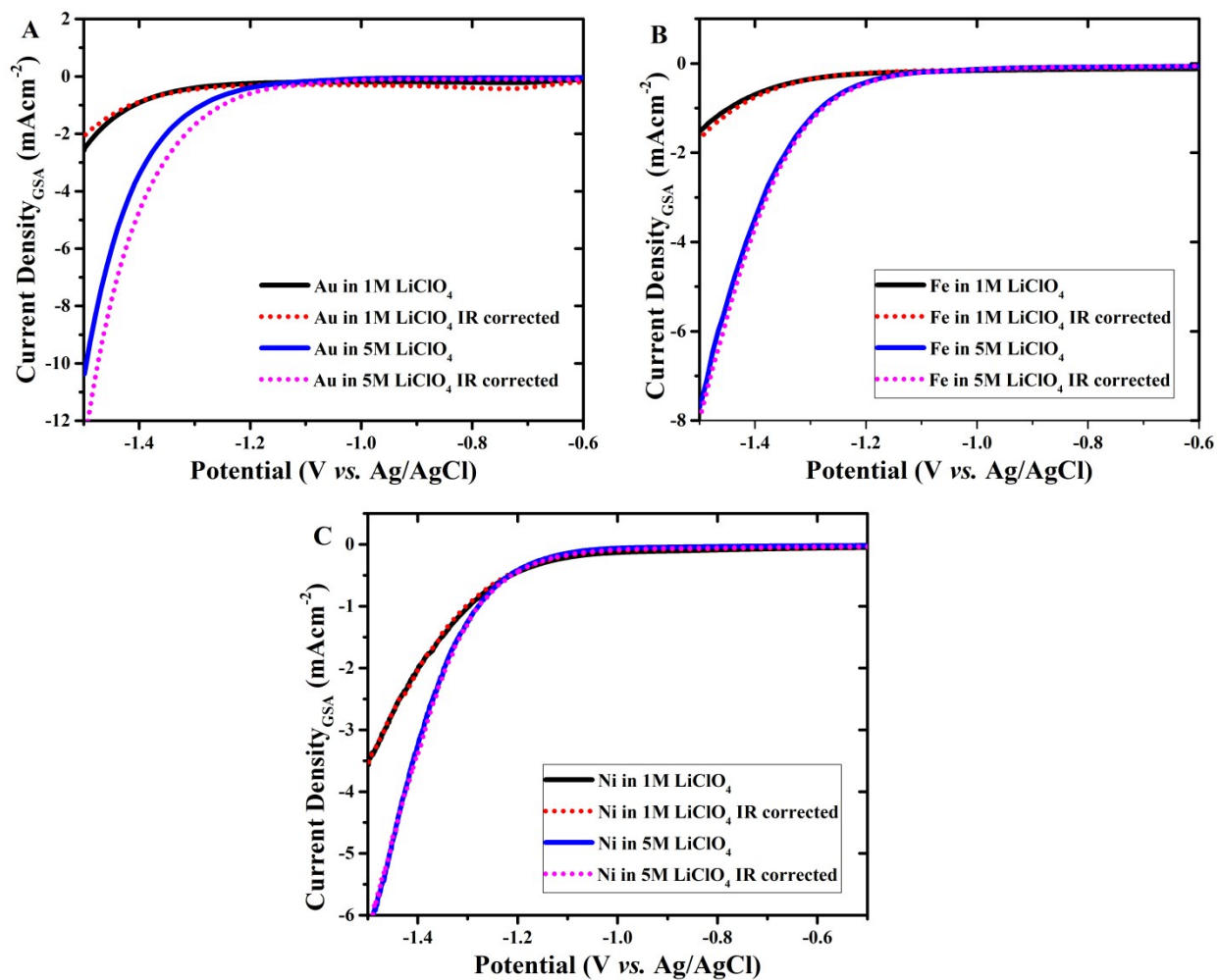


Figure S5: LSVs of (A) Au, (B) Fe and, (C) Ni in LiClO_4 saturated by Argon. Scan rate 50 mV/s.

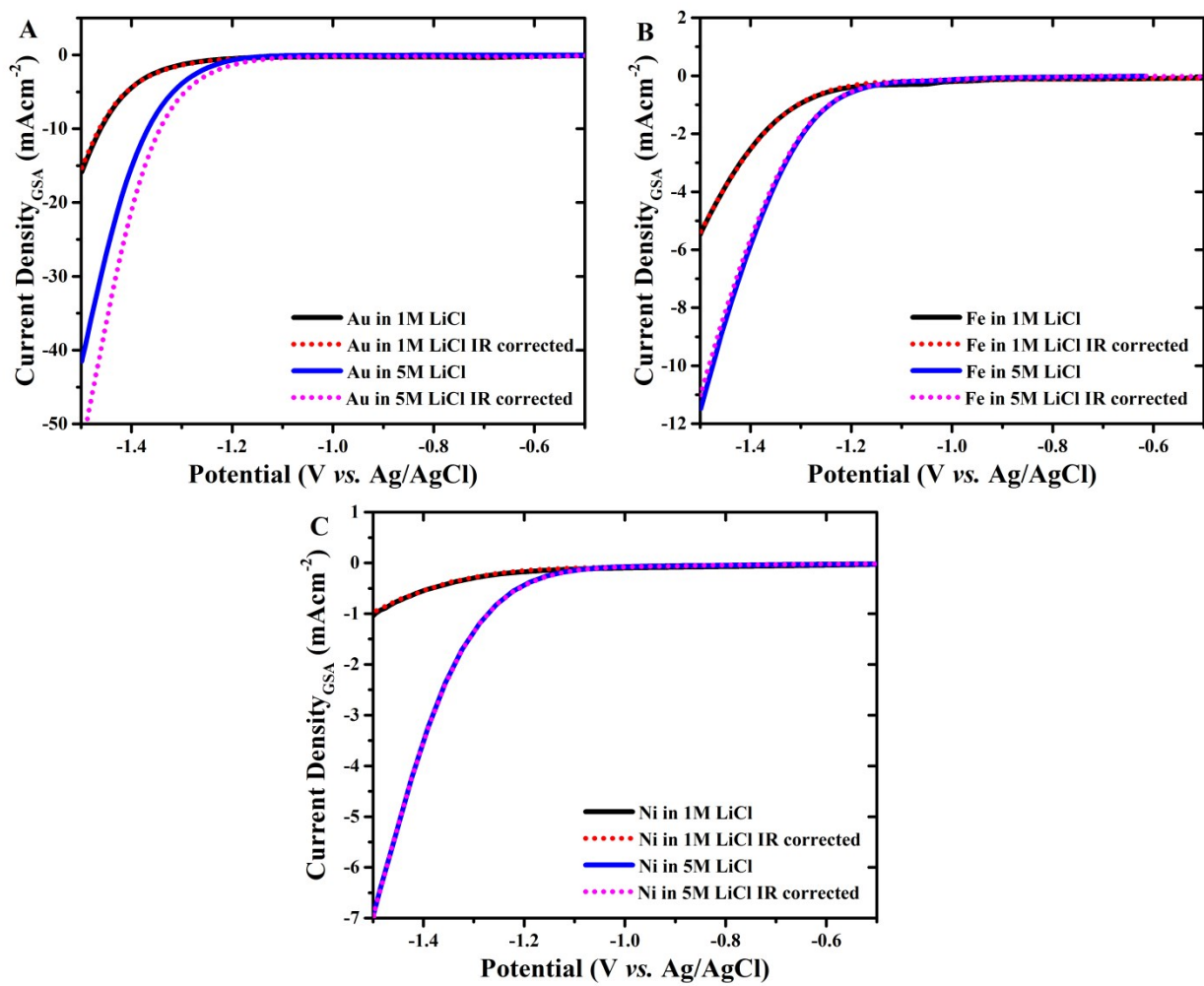


Figure S6: LSVs of (A) Au, (B) Fe and, (C) Ni in LiCl saturated by Argon. Scan rate 50 mV/s.

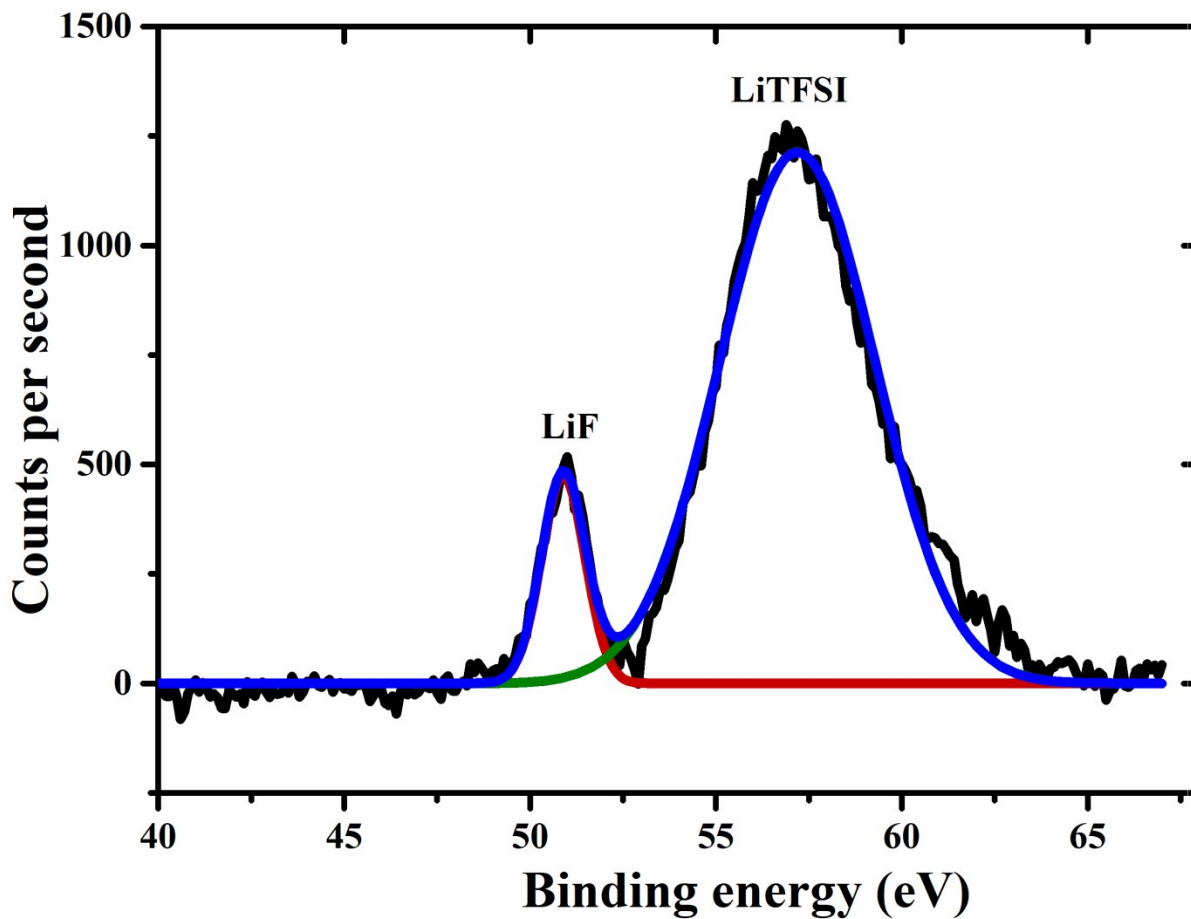


Figure S7: XPS spectra of Li 1s showing the formation of LiF in small amount compared to LiTFSI.¹

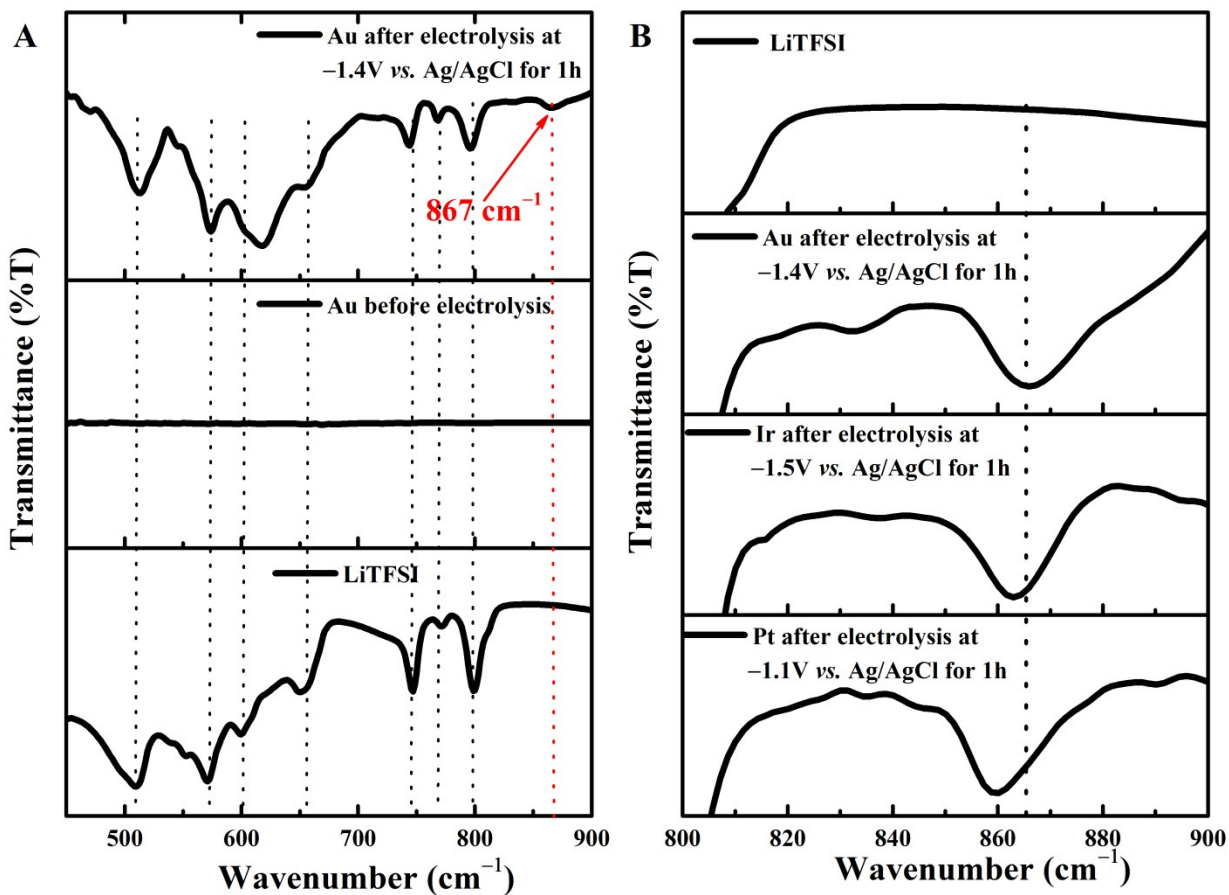


Figure S8: ATR-FTIR spectra of (A) LiTFSI (powder) and Au (foil) surface (before and after electrolysis). The enlarged IR regions showing the presence of LiF in Au, Ir, and Pt are shown in in figure (B), where the electrodes after electrolysis are compared with LiTFSI.

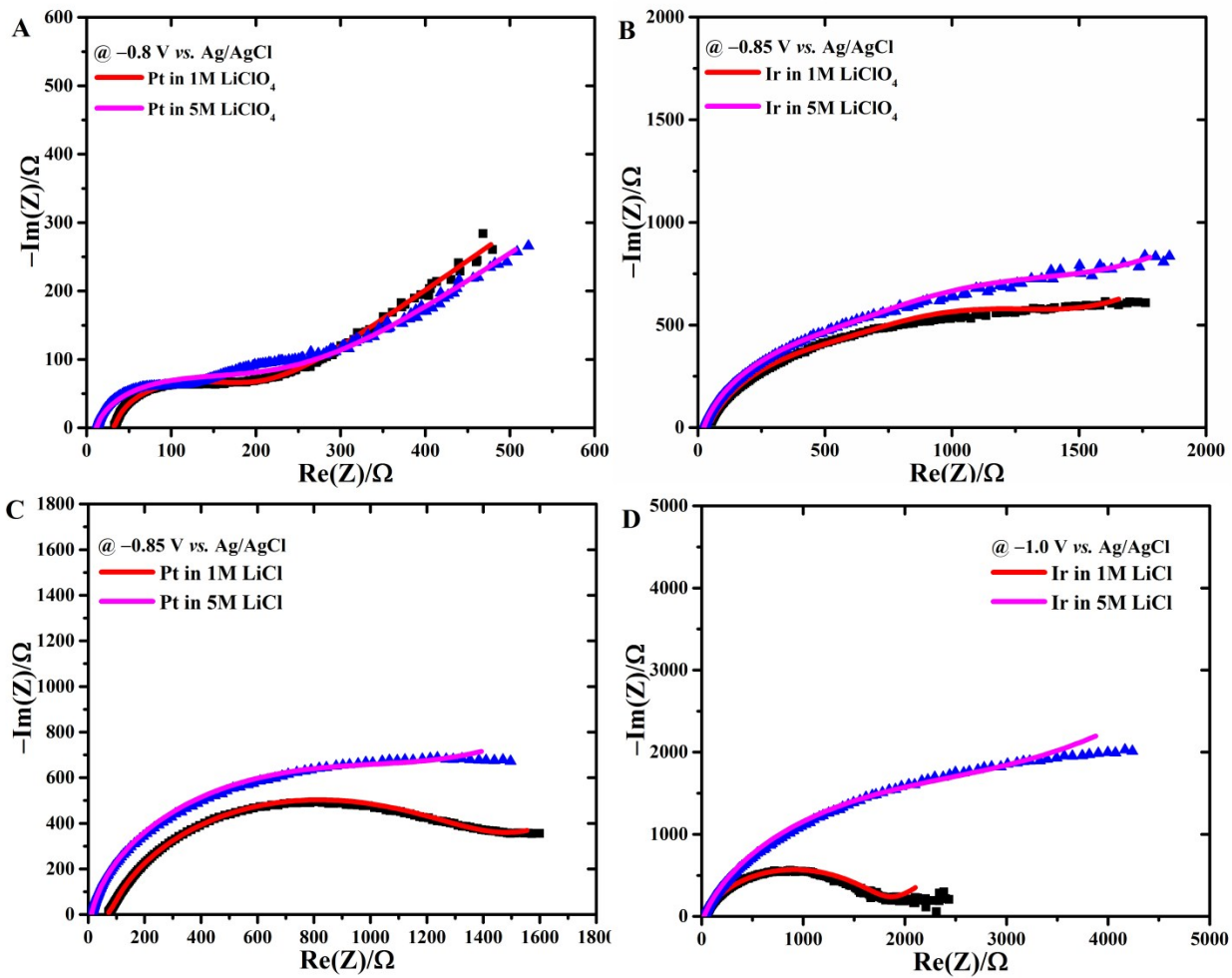


Figure S9: EIS spectra of (A) Pt and (B) Ir in 1M and 5M LiClO₄. EIS spectra of (C) Pt and (D) Ir in 1M and 5M LiCl.

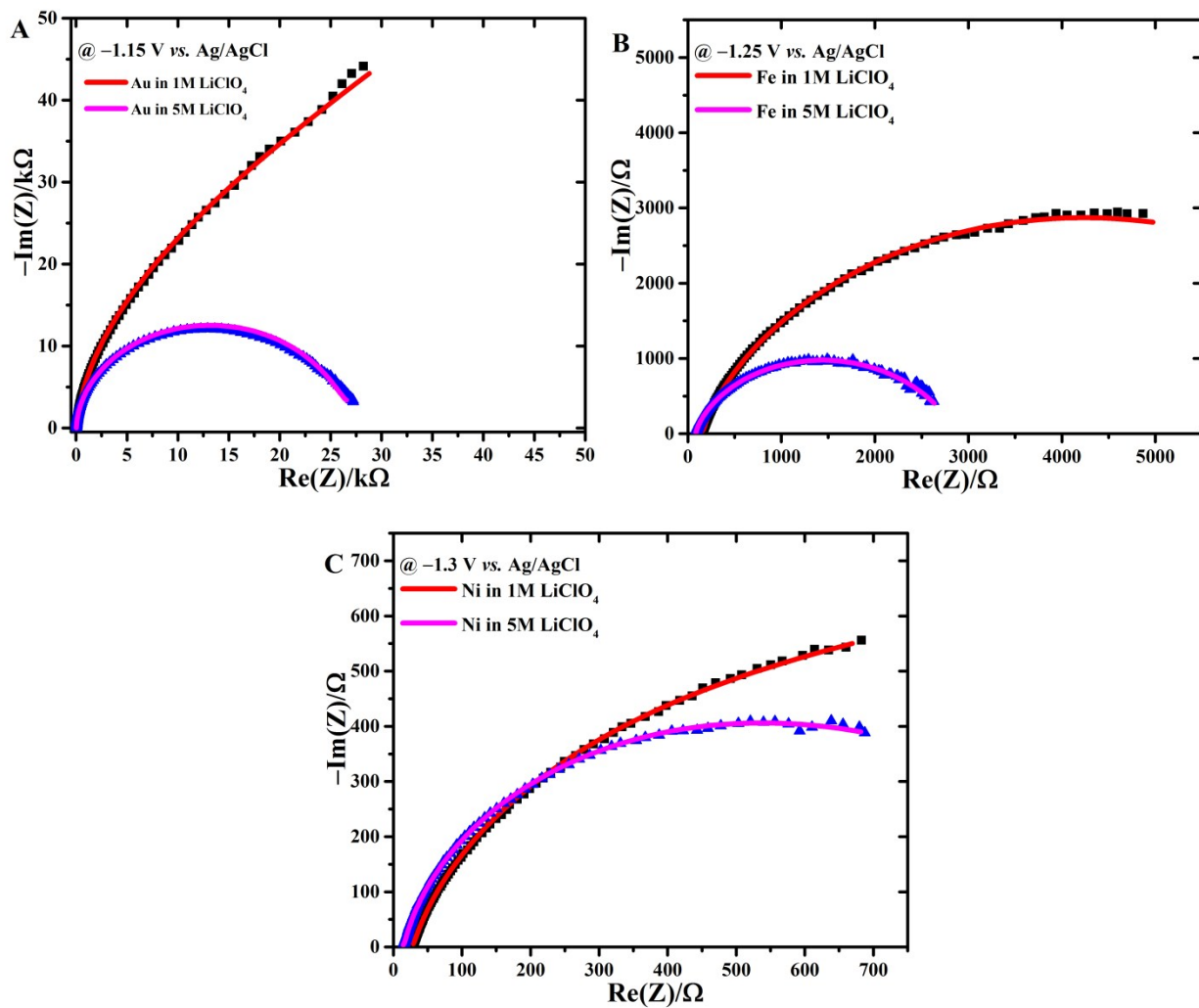


Figure S10: EIS of (A) Au, (B) Fe and, (C) Ni in 1M and 5M LiClO₄.

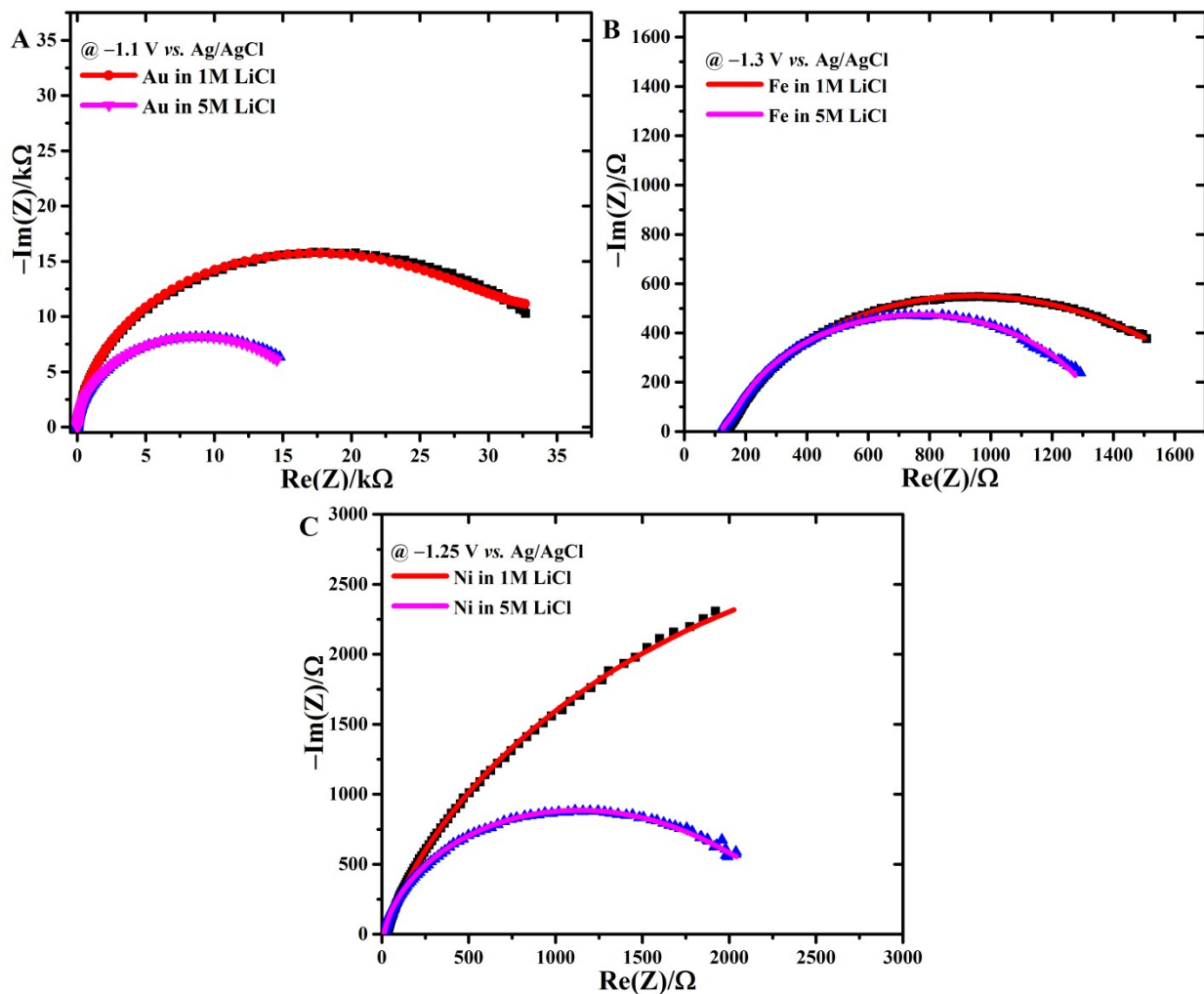


Figure S11: EIS of (A) Au, (B) Fe and, (C) Ni in 1M and 5M LiCl.

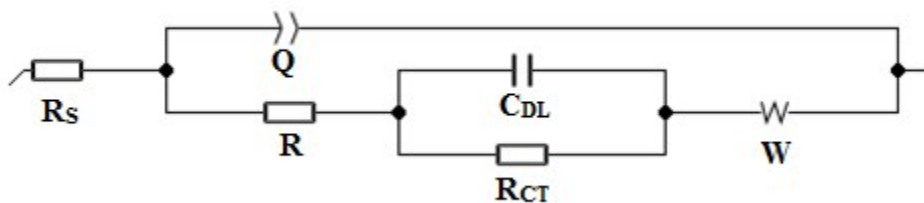


Figure S12: The Randles circuit fitted to the above Nyquist plots.

Table S1: R_s , R , R_{CT} and, C_{DL} values of Pt, Ir, Au, Fe and Ni in 1M and, 5M LiClO₄.

Metals	Pt		Ir		Au		Fe		Ni	
	1M LiCl O ₄	5M LiCl O ₄	1M LiCl O ₄	5M LiCl O ₄	1M LiCl O ₄	5M LiCl O ₄	1M LiCl O ₄	5M LiCl O ₄	1M LiCl O ₄	5M LiCl O ₄
R_s (Ω)	22.3	6.2	41.4	23.04	47.6	17.76	123.7	72.85	26.68	12.66
R (Ω)	12.8	6.8	954.4	1008	764.5	154.6	148.3	33.12	42.6	21.3
R_{CT} (Ω)	249	408	374.2	389	3726 1	2550 3	8240	2774	966	895
C_{DL} (μF or $mFcm^{-2}$)	3.32 Or 47.4	2.19 Or 31.3	41.4 Or 579.1	40.7 Or 572.9	0.16 Or 5.3	0.82 Or 27.3	0.74 10.6	1.03 14.7	0.38 Or 5.43	0.65 Or 9.3

Table S2: R_s , R , R_{CT} and, C_{DL} values of Pt, Ir, Au, Fe and Ni in 1M and, 5M LiCl.

Metals	Pt		Ir		Au		Fe		Ni	
	1M LiCl	5M LiCl	1M LiCl	5M LiCl	1M LiCl	5M LiCl	1M LiCl	5M LiCl	1M LiCl	5M LiCl
R_s (Ω)	68.6	11.27	28.59	22.3	41.9	4.5	134.9	119.6	23	9.1
R (Ω)	230.9	90.79	42.9	22.9	88.23	111.82	212.8	296.4	16.8	3.96
R_{CT} (Ω)	1135	1129	1763	3376	29770	17637	1362	1026	8076	2213
C_{DL} (μF or $mFcm^{-2}$)	0.97 Or 13.9	0.28 Or 4	0.64 Or 9.14	0.21 Or 3	0.3 Or 10	2.1 Or 70	0.7 Or 10	1.74 Or 24.8	1.46 Or 20.8	1.5 Or 21.43

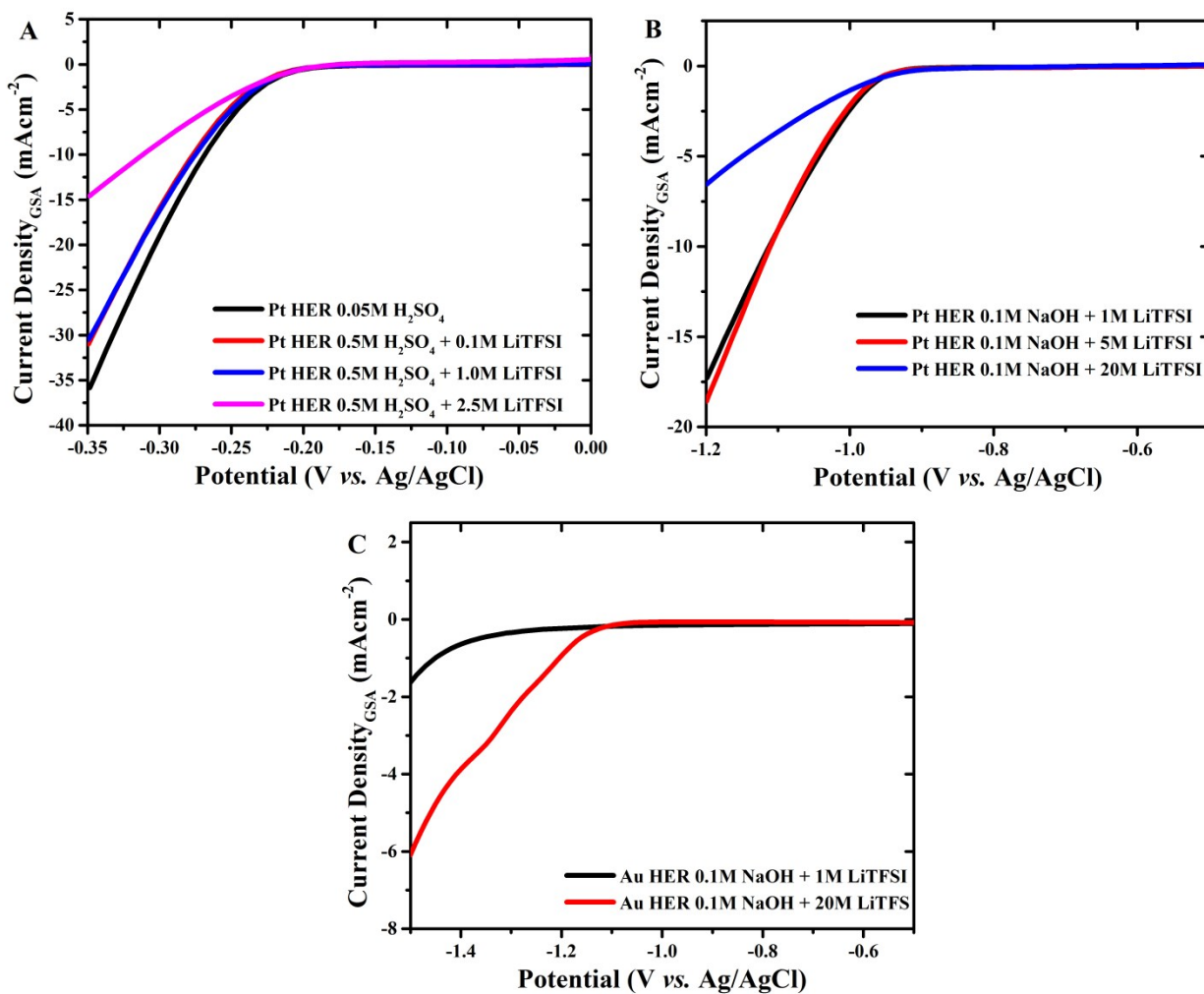


Figure S13: LSVs of Pt in different concentration of LiTFSI in (A) 0.5M H₂SO₄ and, (B) 0.1M NaOH. (C) LSVs of Au in different concentration of LiTFSI in 0.1M NaOH. Scan rate 50 mV/s. Graphite rod is used as counter.

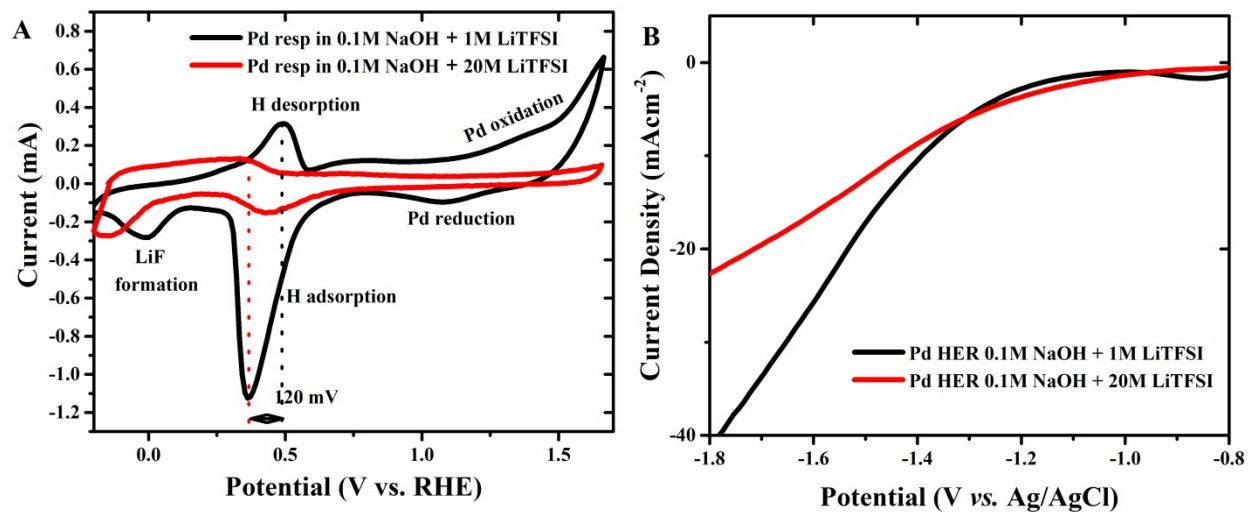


Figure S14: The CVs (A) and LSVs (B) with Palladium (Pd) in different LiTFSI concentrations in 0.1M NaOH saturated by Argon. Scan rate is 50 mV/s. Graphite rod is used as counter electrode.

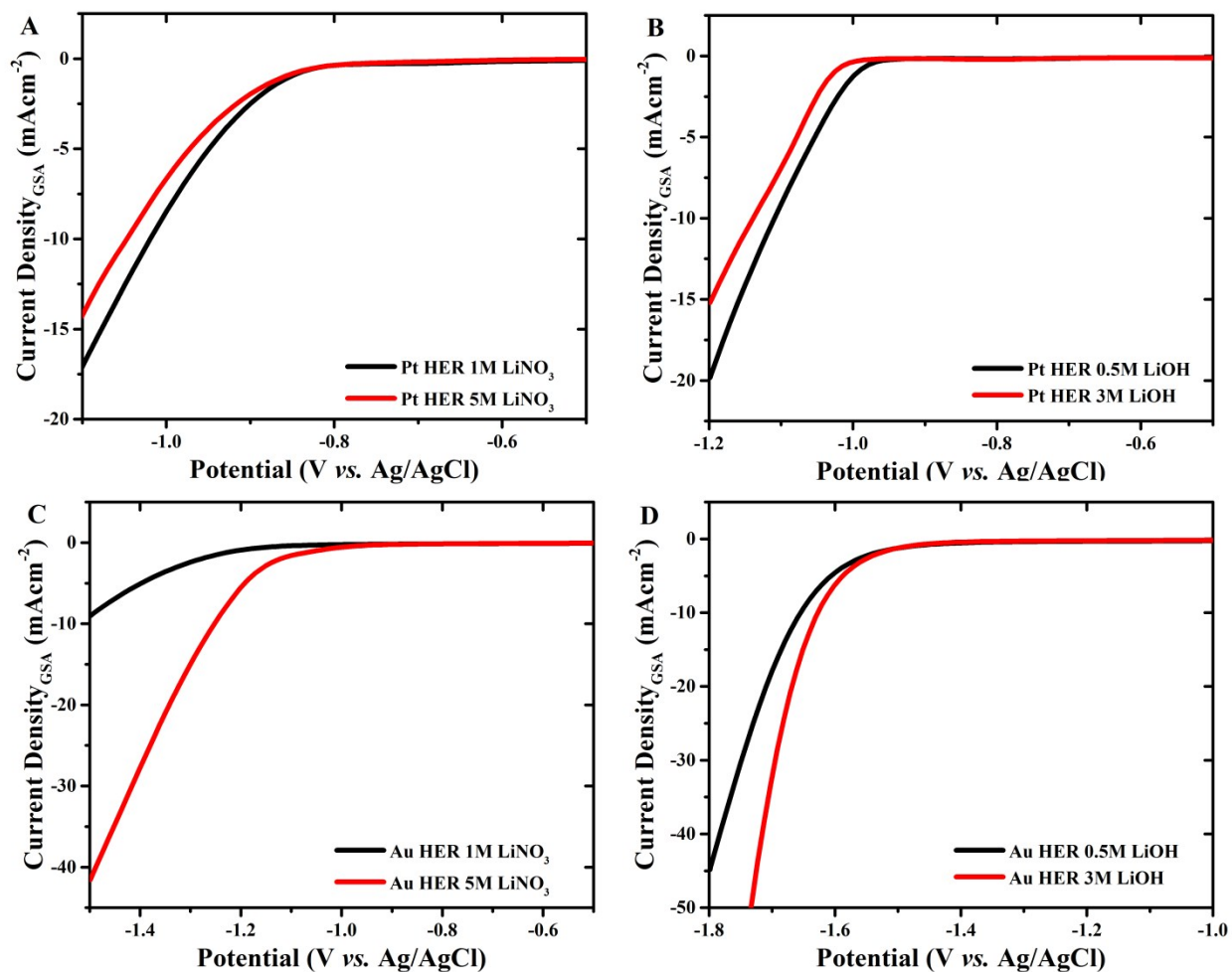


Figure S15: LSVs of Pt in different concentration of (A) LiNO_3 and, (B) LiOH and, LSVs of Au in different concentration of (C) LiNO_3 and (D) LiOH saturated by Argon. Scan rate 50 mV/s. Graphite rod is used as counter.

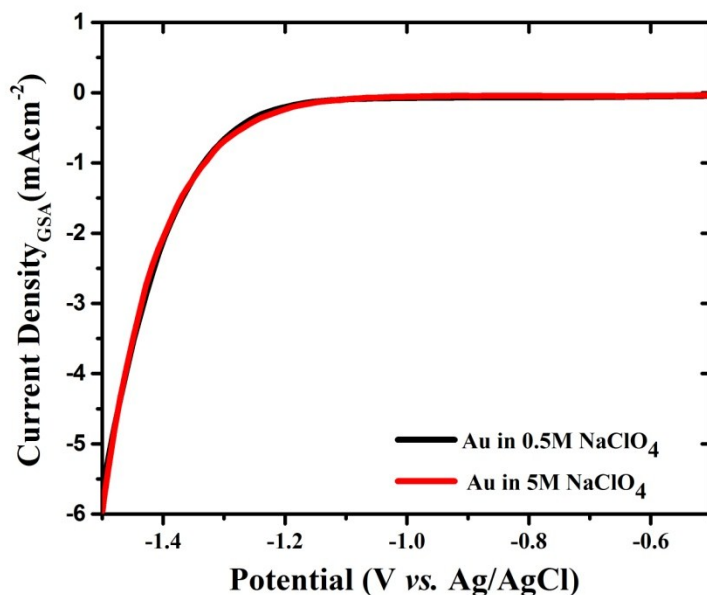


Figure S16: LSVs of Au in different concentration of NaClO₄ saturated by Argon. Scan rate 50 mV/s. Pt is used as counter electrode.

Electrochemically active surface area (ECSA):

Pt, Ir:

Electrochemically active surface area (ECSA) of both Pt, Ir were calculated by taking under potential deposition region of the cyclic voltammogram in Argon saturated 0.1M KOH (sigma aldrich) medium. The cyclic voltammograms were measured at a scan rate 200 mVps using Ag/AgCl and graphite rod were used as reference and counter electrode respectively. The charge densities associated to monolayer hydrogen coverage are 210 $\mu\text{C}/\text{cm}^2$ and 218 $\mu\text{C}/\text{cm}^2$ for Pt² and Ir³ respectively.

Au:

To calculate the electrochemically active surface area (ECSA) of Au, Au was electro-cycled in Argon saturated 0.5M H₂SO₄ from 0V to 1.6V vs. Ag/AgCl at 200 mV/s. For ECSA calculation the reduction peak at 0.8V vs. Ag/AgCl due to reduction of AuO corresponding charge density is 390 $\mu\text{C}/\text{cm}^2$.¹

Ni:

For the ECSA calculation of Ni, Ni was electro-cycled from 0V to 0.5V vs. Ag/AgCl in Argon saturated 0.1M KOH at 200 mV/s. The reduction peak of Ni(OH)₂ at V vs. Ag/AgCl corresponding charge density of 514 $\mu\text{C}/\text{cm}^2$ was taken for active surface area calculation.⁴

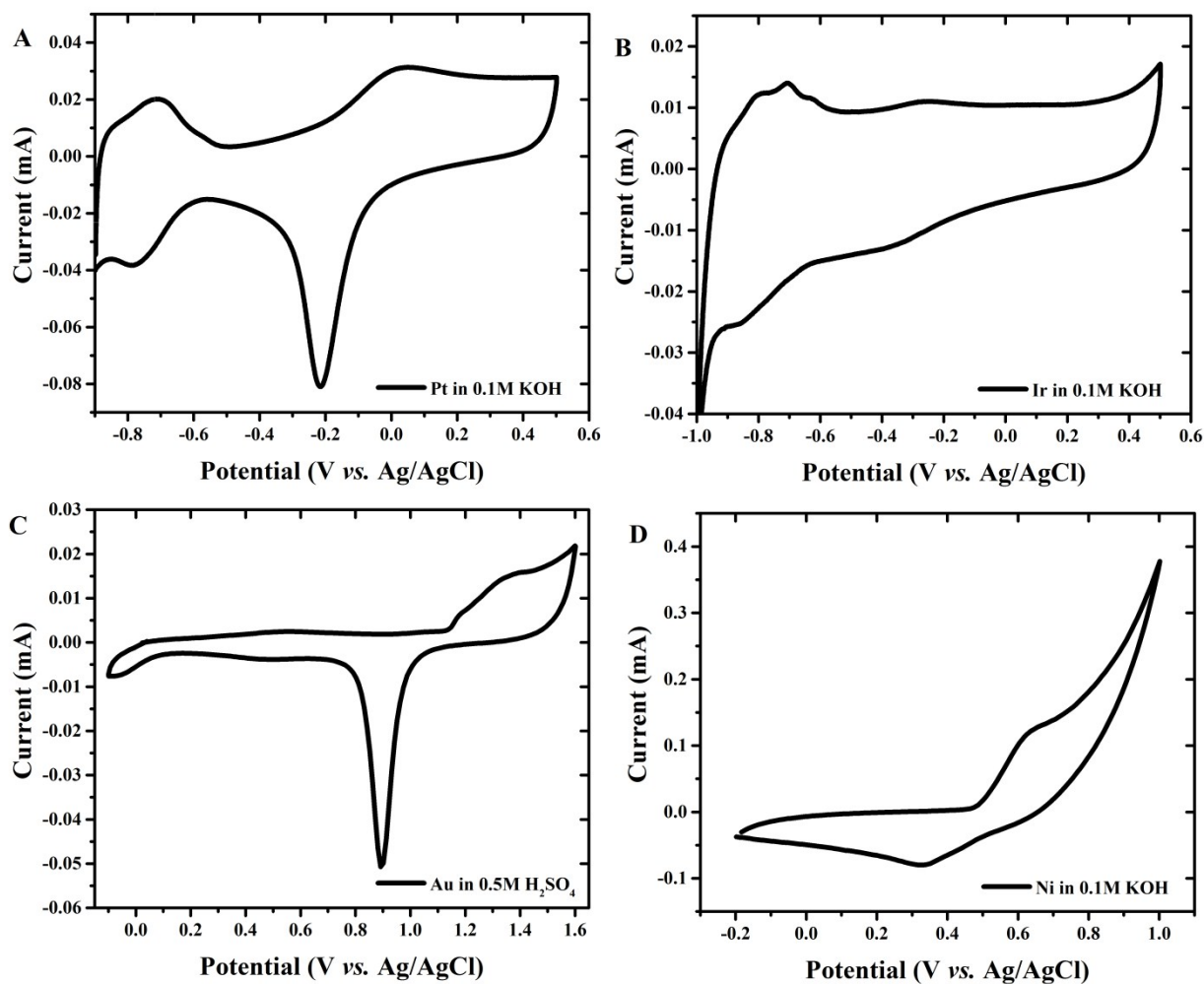


Figure S17: ECSA calculation of (A) Pt, (B) Ir, (C) Au and (D) Ni. Scan rate 200 mV/s. Graphite rod is used as counter.

References:

- 1 A. Guha, S. Narayanaru and T. N. Narayanan, *ACS Appl. Energy Mater.*, 2018, **1**, 7116–7122.
- 2 A. Guha, T. Veettil Vineesh, A. Sekar, S. Narayanaru, M. Sahoo, S. Nayak, S. Chakraborty and T. N. Narayanan, *ACS Catal.*, 2018, **8**, 6636–6644.
- 3 J. Zheng, Z. Zhuang, B. Xu and Y. Yan, *ACS Catal.*, 2015, **5**, 4449–4455.
- 4 W. Sheng, M. Myint, J. G. Chen and Y. Yan, *Energy Environ. Sci.*, 2013, **6**, 1509–1512.