Overcoming passivation through improved mass transport in dense ionic fluids

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Supplementary Information

Table S1: Source, purity, and diameter of the metal wires used to form the working electrodes and pseudo reference electrodes.

Metal Wire	Purity	Source	Diameter (mm)
Copper	99.00%	RS	1.25
Nickel	98.00%	VWR	1.00
Cobalt	99.995%	Alfa-Aesar	1.00
Silver	99.90%	Alfa-Aesar	0.50
Aluminium	>98.00%	Unicorn Metals	3.00
Titanium	Grade 5 >98.00%	Unicorn Metals	3.00

Table S2: Literature values for viscosity and conductivity of the three choline chloride systems investigated.

Solvent	[Cl⁻] / mol kg⁻¹ of total solvent	Density / g cm⁻³	Viscosity / mPa s	Conductivity / mS cm⁻¹	Literature
ChCl:2EG	3.79	1.12	37	7.61	lit *
1:3 Brine	5.16	1.097(4)	14.08(6)	43.3(3)	lit **
1:6.85 Brine	3.79	1.057(5)	4.19(9)	83.1(6)	this work

* Data taken from T. Isono, *J. Chem. Eng. Data*, 1984, **29**, 45-52
** Data taken from G. Zante et al, *Angew. Chem. Int. Ed. Eng.*, 2023, **62**, e202311140

Table S3: Table showing the parameters used for calculation of the copper(I) concentration at the solvent-electrode interface at the point of passivation for three different ChCl systems. E_{ox} is the onset potential of copper oxidation, E_{pass} is the potential at which the peak current is observed under silent conditions and $[Cu^+]_{x=0}$ is the concentration of Cu(I) at the electrode interface prior to the onset of electrode passivation.

ChCl:2EG, $[Cl^-]$ = 4.25 mol dm^{-3}

Voltage scan rate / V s^{-1}	**$D(Cu^+)$ / m^2 s^{-1} ***	**Peak anodic current density / A m^{-2}**	**E_{ox}-E_{pass} / V**	**$[Cu^+]_{x=0}$ / mol dm^{-3}**	**$[Cu^+]_{x=0}$:$[Cl^-]_{bulk}$**
0.01	8.57×10^{-12}	393	0.44	4.61	1.09
0.05	8.57×10^{-12}	823	0.66	5.29	1.25
0.1	8.57×10^{-12}	1172	0.76	5.72	1.35

1:3 ChCl:water, $[Cl^-]$ = 5.70 mol dm^{-3}

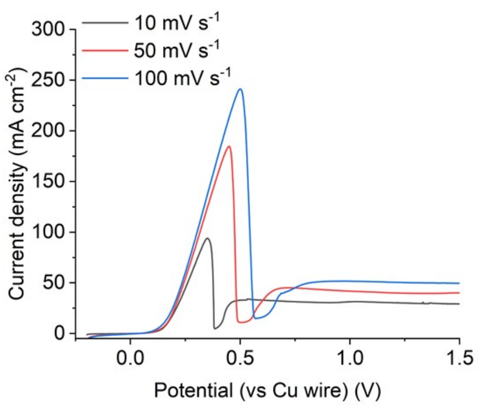
Scan rate / V s^{-1}	**$D(Cu^+)$ / m^2 s^{-1} †**	**Peak anodic current density / A m^{-2}**	**E_{ox}-E_{pass} / V**	**$[Cu^+]_{x=0}$ / mol dm^{-3}**	**$[Cu^+]_{x=0}$:$[Cl^-]_{bulk}$**
0.01	1.55×10^{-11}	695	0.29	4.94	0.87
0.05	1.55×10^{-11}	1308	0.42	4.99	0.88
0.1	1.55×10^{-11}	1667	0.49	4.86	0.86

1:6.85 ChCl:water, $[Cl^-]$ = 4.02 mol dm^{-3}

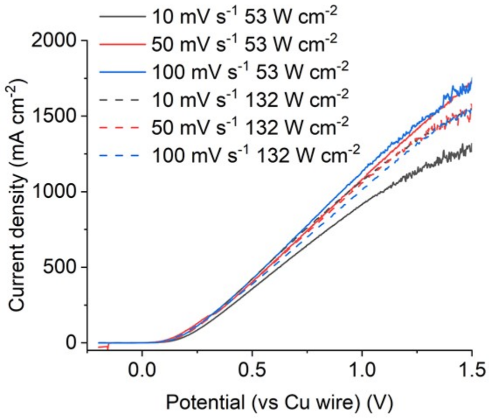
Scan rate / V s^{-1}	**$D(Cu^+)$ / m^2 s^{-1} ‡**	**Peak anodic current density / A m^{-2}**	**E_{ox}-E_{pass} / V**	**$[Cu^+]_{x=0}$ / mol dm^{-3}**	**$[Cu^+]_{x=0}$:$[Cl^-]_{bulk}$**
0.01	1.09×10^{-10}	940	0.22	1.69	0.42
0.05	1.09×10^{-10}	1847	0.32	1.79	0.45
0.1	1.09×10^{-10}	2412	0.39	1.83	0.46

* Diffusion coefficient from A. Y. M. Al-Murshedi, et al., *Trans. IMF*, 2019, **97**, 321-329
† Diffusion coefficient from G. Zante, et al., *Angew. Chem. Int. Ed. Eng.*, 2023, **62**, e202311140
‡ Diffusion coefficient estimated via interpolation of data reported in G. Zante, et al., *Angew. Chem. Int. Ed. Eng.*, 2023, **62**, e202311140.

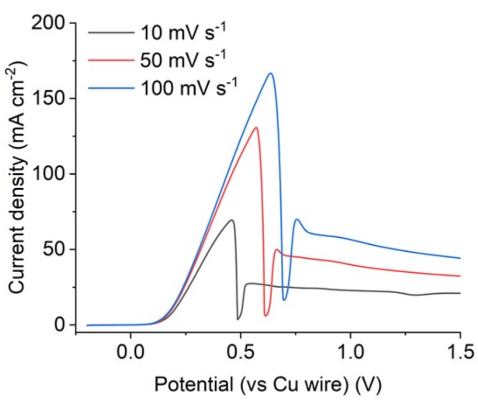
a) 1:6.85 ChCl:H_2O (silent)



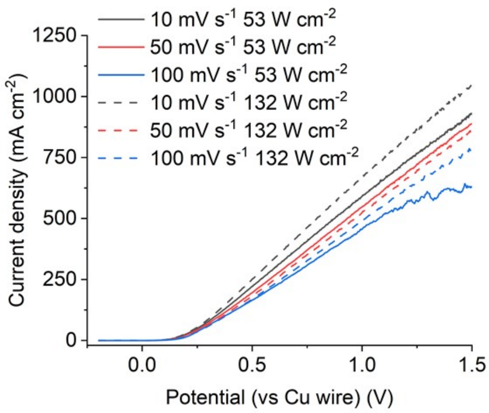
b) 1:6.85 ChCl:H_2O (ultrasonic)



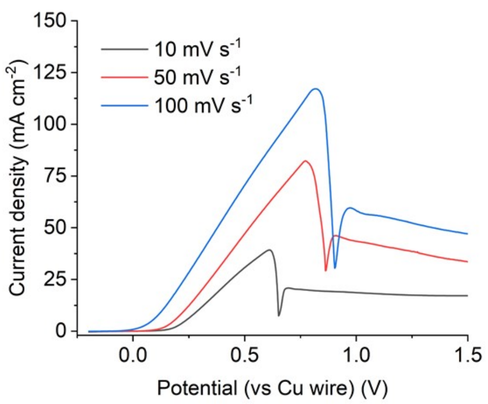
c) 1:3 ChCl:H_2O (silent)



d) 1:3 ChCl:H_2O (ultrasonic)



e) ChCl:2EG (silent)



f) ChCl:2EG (ultrasonic)

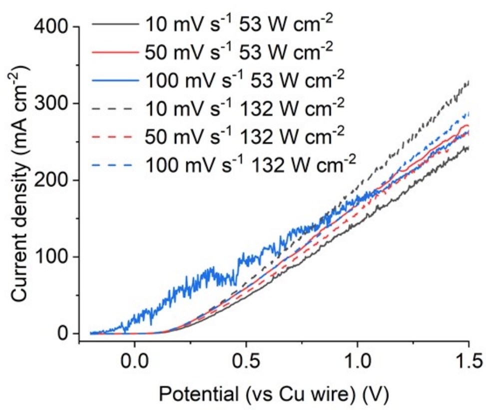


Figure S1: Effect of scan rate on the LSVs of a copper disc working electrode under silent and ultrasonic conditions (53 and 132 W cm^{-2}). The quasi-reference electrode was a copper wire, and the counter electrode was an iridium oxide-coated titanium mesh. Measurements were carried out at room temperature.

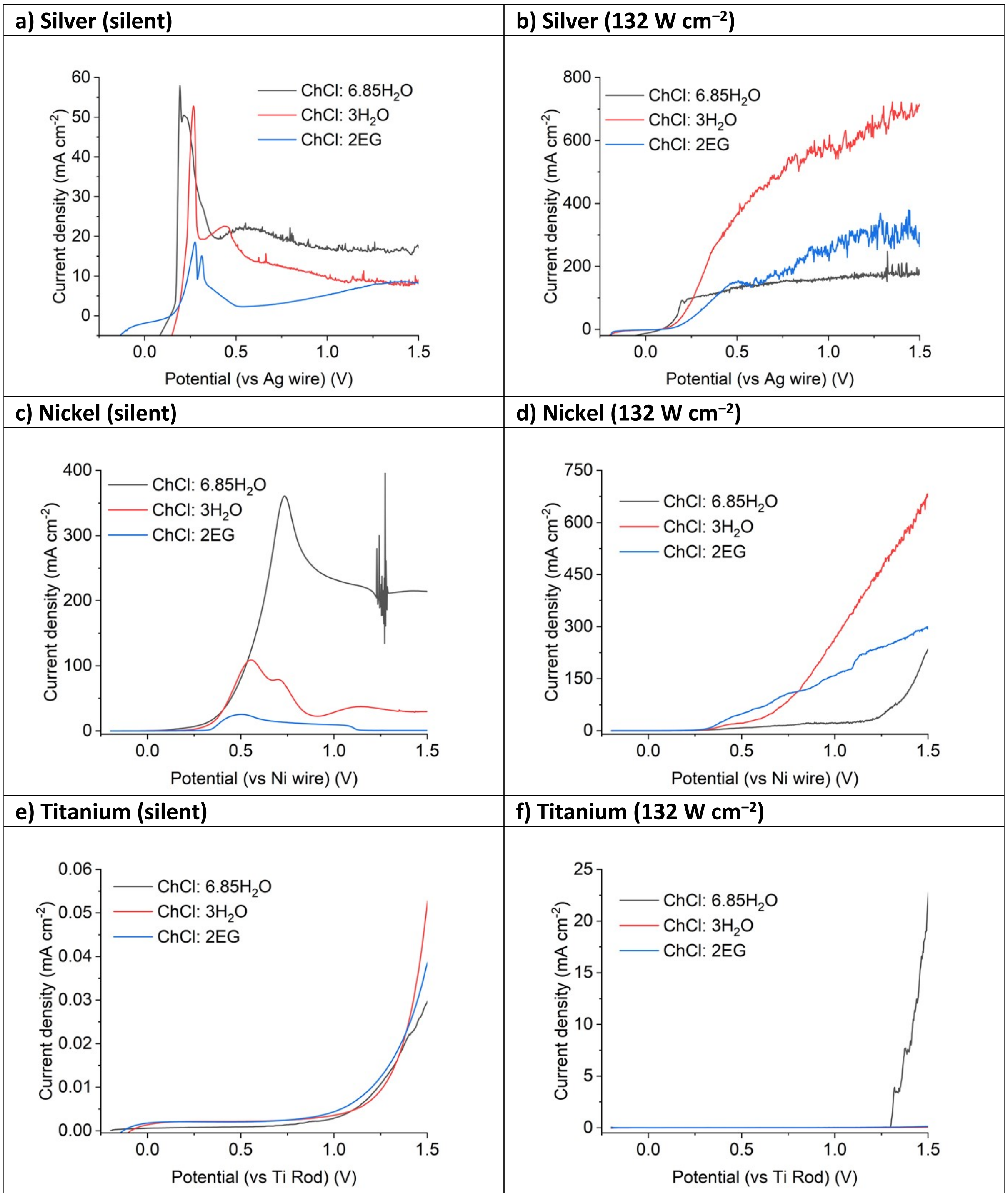


Figure S2: Linear sweep voltammograms of a, b) silver, c, d) nickel, and e, f) titanium disc working electrodes in ChCl:2EG and two different ChCl brines, under a, c, e) silent, and b, d, f) 132 W cm^{-2}. The reference electrode was the same metal as the working electrode, and the scan rate was 10 mV s^{-1}. First scans presented only.

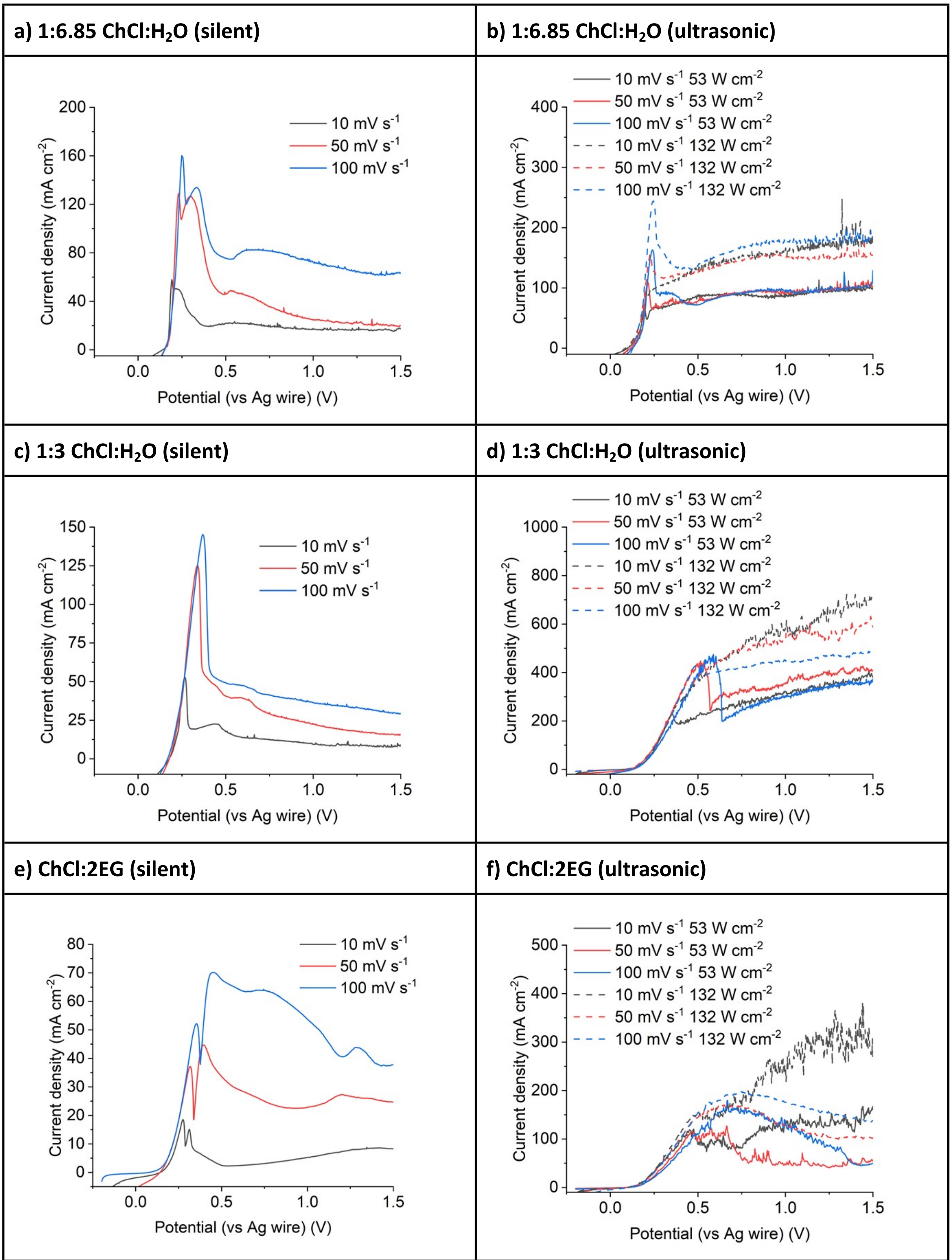


Figure S3: Effect of scan rate on the LSVs of a silver disc working electrode under silent and ultrasonic conditions (53 and 132 W cm^{-2}). The quasi-reference electrode was a silver wire, and the counter electrode was an iridium oxide-coated titanium mesh. Measurements were carried out at room temperature.

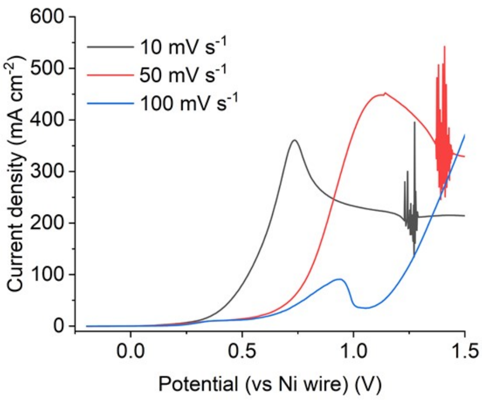
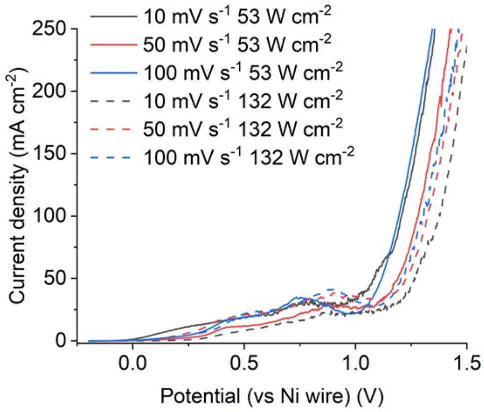
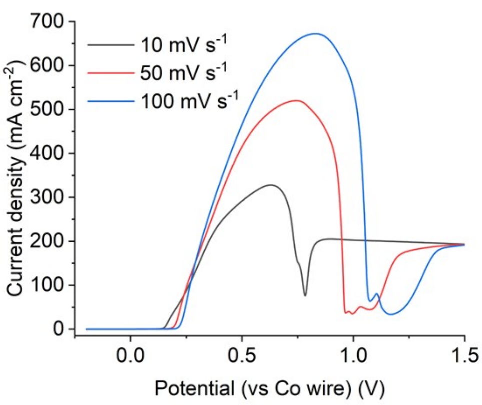
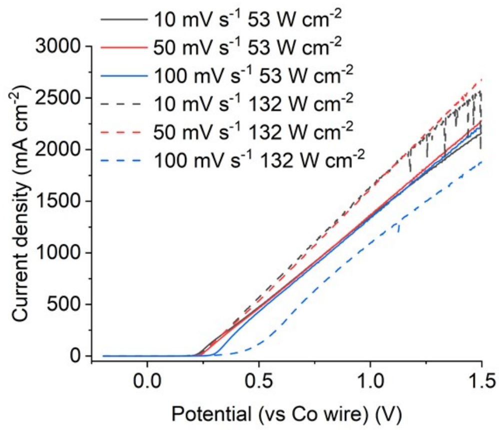
a) 1:6.85 ChCl:H_2O (silent)	b) 1:6.85 ChCl:H_2O (ultrasonic)
	

Figure S4: Effect of scan rate on the LSVs of a nickel disc working electrode under silent and ultrasonic conditions (53 and 132 W cm^{-2}). The quasi-reference electrode was a nickel wire, and the counter electrode was an iridium oxide-coated titanium mesh. Measurements were carried out at room temperature.

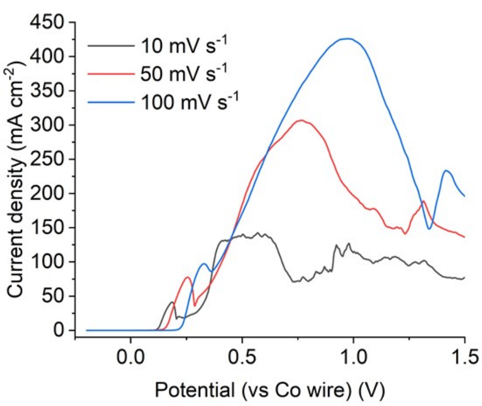
a) 1:6.85 ChCl:H_2O (silent)



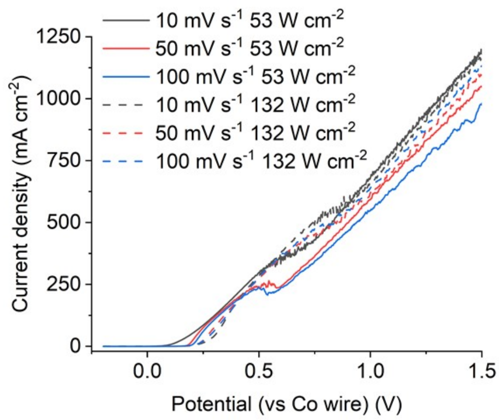
b) 1:6.85 ChCl:H_2O (ultrasonic)



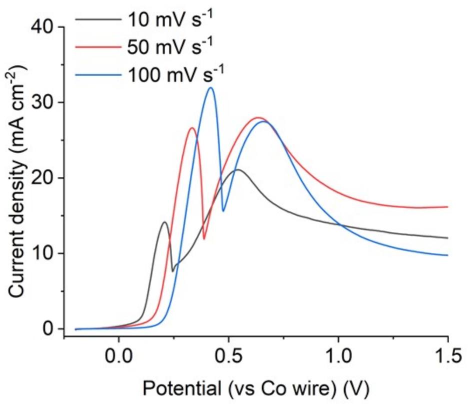
c) 1:3 ChCl:H_2O (silent)



d) 1:3 ChCl:H_2O (ultrasonic)



e) ChCl:2EG (silent)



f) ChCl:2EG (ultrasonic)

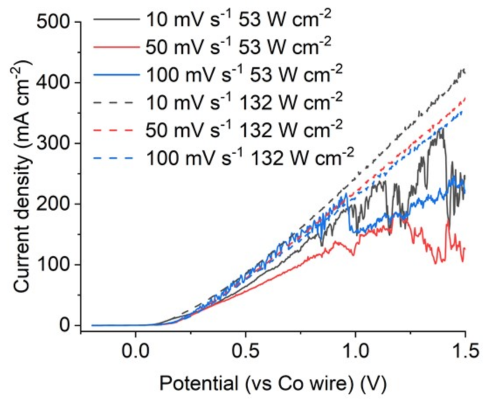
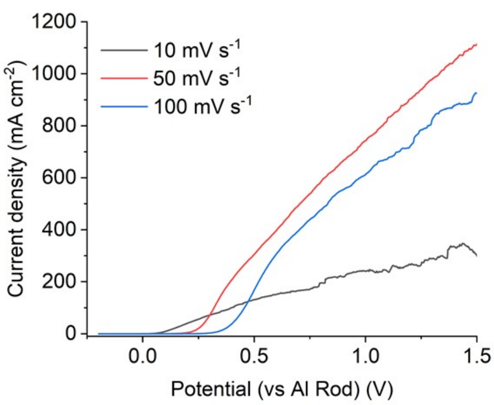
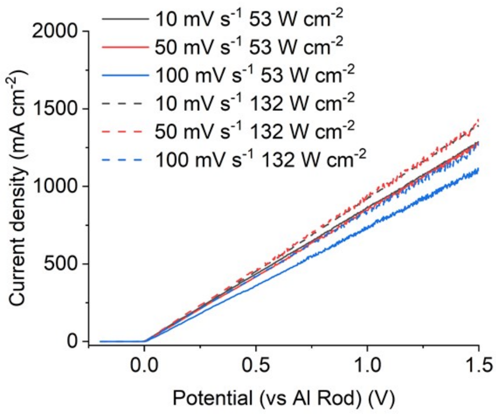


Figure S5: Effect of scan rate on the LSVs of a cobalt disc working electrode under silent and ultrasonic conditions (53 and 132 W cm^{-2}). The quasi-reference electrode was a cobalt wire, and the counter electrode was an iridium oxide-coated titanium mesh. Measurements were carried out at room temperature.

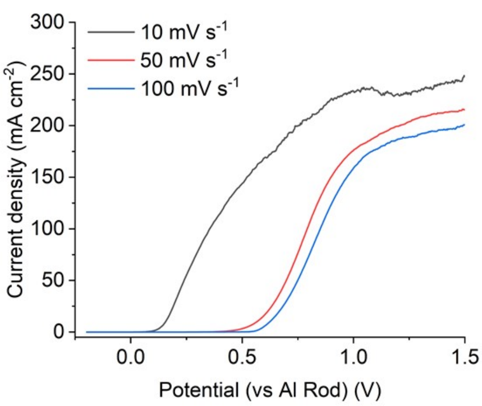
a) 1:6.85 ChCl:H_2O (silent)



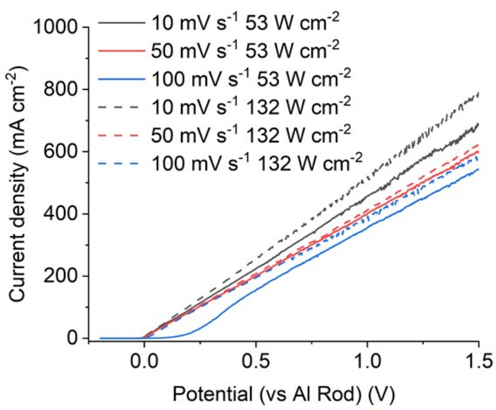
b) 1:6.85 ChCl:H_2O (ultrasonic)



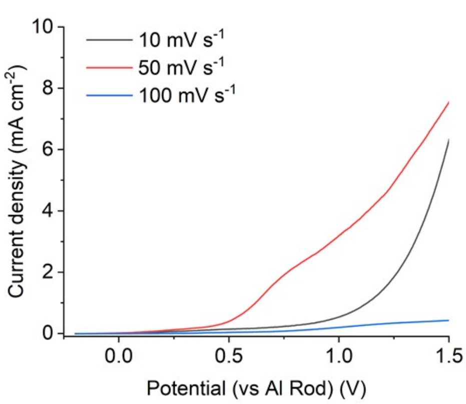
c) 1:3 ChCl:H_2O (silent)



d) 1:3 ChCl:H_2O (ultrasonic)



e) ChCl:2EG (silent)



f) ChCl:2EG (ultrasonic)

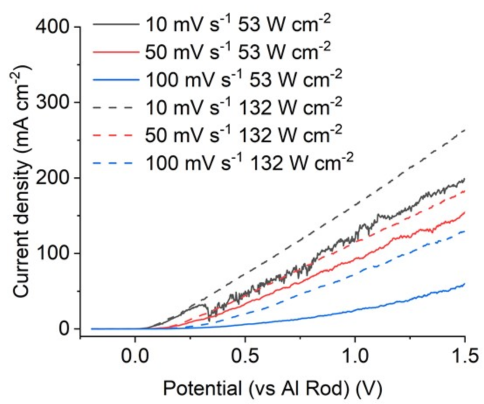
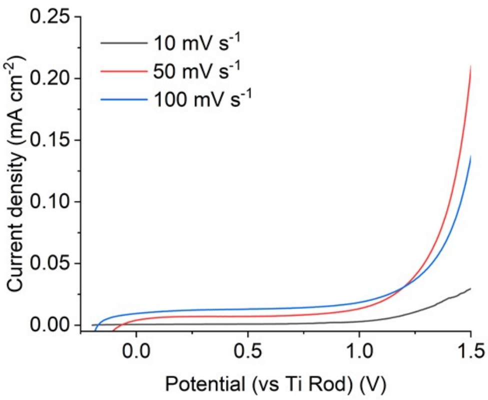
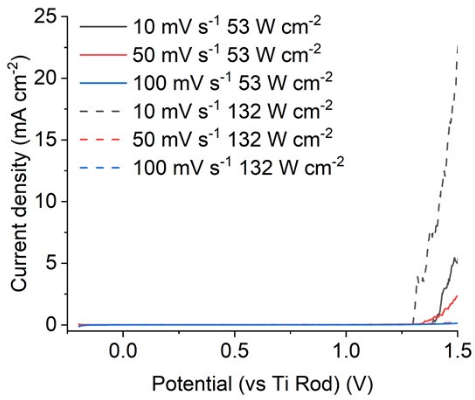


Figure S6: Effect of scan rate on the LSVs of an aluminium disc working electrode under silent and ultrasonic conditions (53 and 132 W cm^{-2}). The quasi-reference electrode was an aluminium wire, and the counter electrode was an iridium oxide-coated titanium mesh. Measurements were carried out at room temperature.

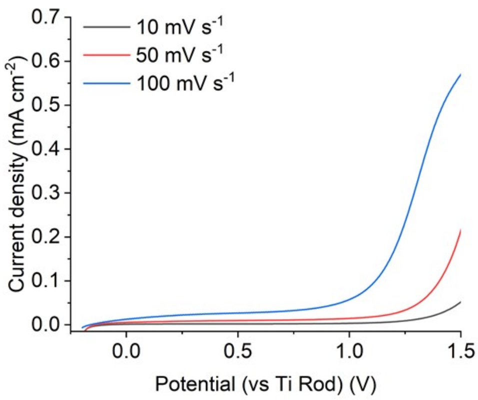
a) 1:6.85 $ChCl:H_2O$ (silent)



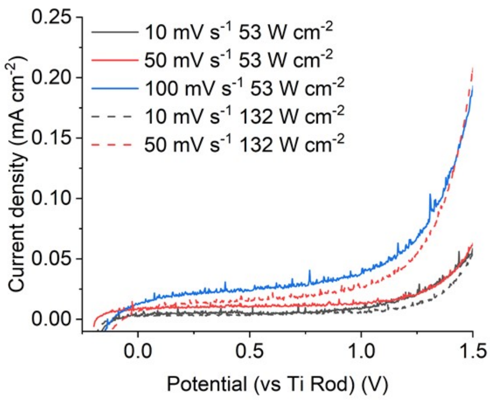
b) 1:6.85 $ChCl:H_2O$ (ultrasonic)



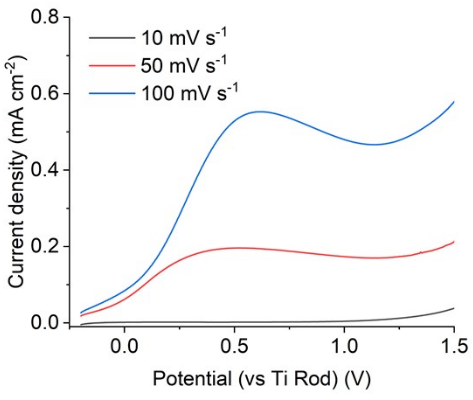
c) 1:3 $ChCl:H_2O$ (silent)



d) 1:3 $ChCl:H_2O$ (ultrasonic)



e) ChCl:2EG (silent)



f) ChCl:2EG (ultrasonic)

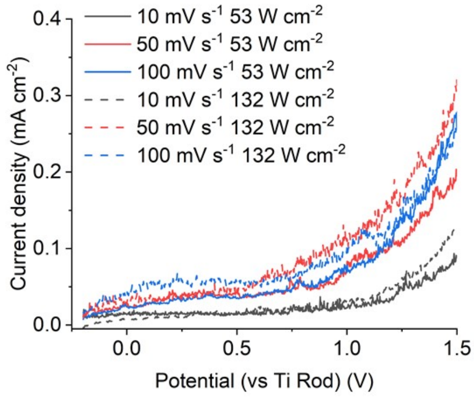
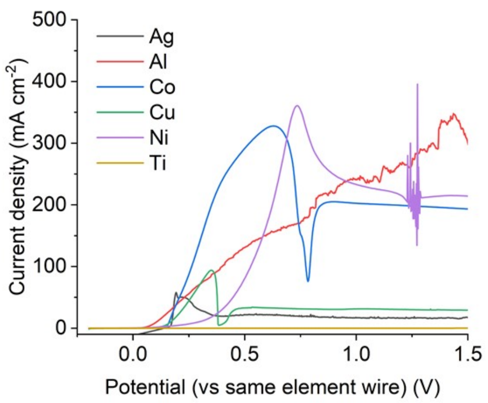
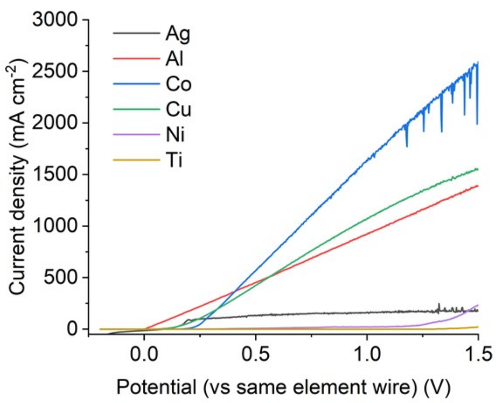


Figure S7: Effect of scan rate on the LSVs of a titanium disc working electrode under silent and ultrasonic conditions (53 and 132 W cm^{-2}). The quasi-reference electrode was a titanium wire, and the counter electrode was an iridium oxide-coated titanium mesh. Measurements were carried out at room temperature.

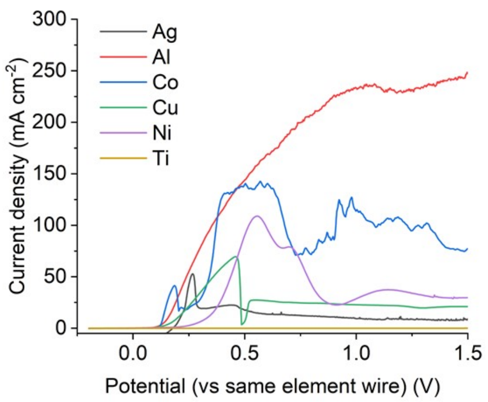
a) 1:6.85 ChCl:H2O (silent)



b) 1:6.85 ChCl:H2O (132 W cm^{-2})



c) 1:3 ChCl:H2O (silent)



d) 1:3 ChCl:H2O (132 W cm^{-2})

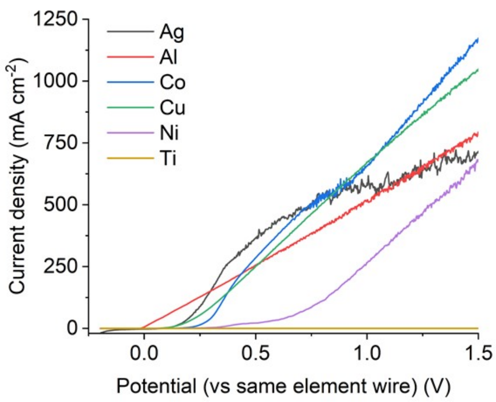


Figure S8: LSVs of the six metals investigated in ChCl:6.85H_2O and ChCl:3H_2O, under a, c) silent conditions, and b, d) 132 W cm^{-2} ultrasound. The scan rate was 10 mV s^{-1}, with a quasi-reference electrode made from the same metal as the metal under investigation.