Supporting information

Mixed-Anion Electrolytes: From Bulk Speciation to Interfacial Dynamics in Divalent Metal Electrodeposition

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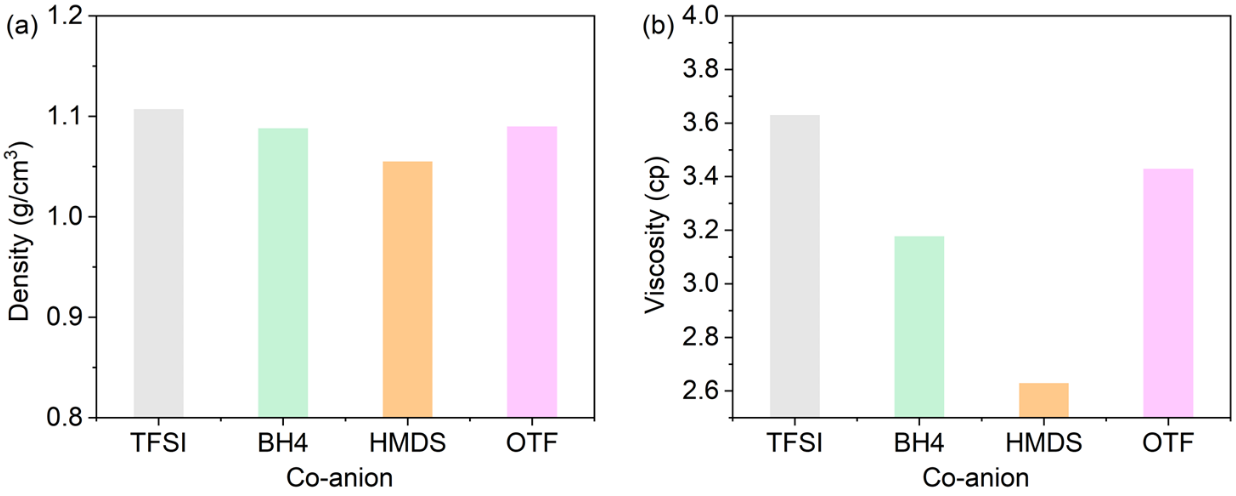

Figure S1. The density and viscosity of each electrolyte measured at 23ºC.

Table S1. The relative ratios for possible solvation species in the electrolyte calculated from negative ESI-MS spectrum. The assigned stoichiometry provides the closest match to the observed m/z; however, a small mass discrepancy may remain. Given the known behavior of Mg–glyme–anion clusters in ESI-MS, the possible solvation species is therefore reported as a tentative assignment for each electrolyte.

Anions	mass (m/z)	Possible solvation species	Ratio (%)
TFSI	280	$[TFSI]^-$	100
$TFSI+BH_4$	280	$[TFSI]^-$	62.59
	566.6	$TFSI(G2)_2(H_2O)]-$	12.1
	598.6	$[Mg(TFSI)_2(BH_4)]-$	4.11
	616.1	$[Mg(TFSI)_2(BH_4)(H_2O)]-$	1.66
	649.1	$[Mg(TFSI)_4(G2)]^{2-}$	19.54
TFSI+HMDS	280	$[TFSI]^-$	59.34
	566.8	$TFSI(G2)_2(H_2O)]-$	2.54
	578.2	$[Mg(HMDS)_3(H_2O)_4]-$	27.86
	649.1	$[Mg(TFSI)_4(G2)]^{2-}$	2.59
	863.9	$[Mg(TFSI)_3]^-$	7.66
TFSI+OTf	280	$[TFSI]^-$	31.59
	566.5	$TFSI(G2)_2(H_2O)]^-$	12.7
	601.8	$[Mg(TFSI)(OTf)_2]^-$	0.88
	732.3	$[Mg(TFSI)_2(OTf)]^-$	11.77
	863.9	$[Mg(TFSI)_3]^-$	42.95

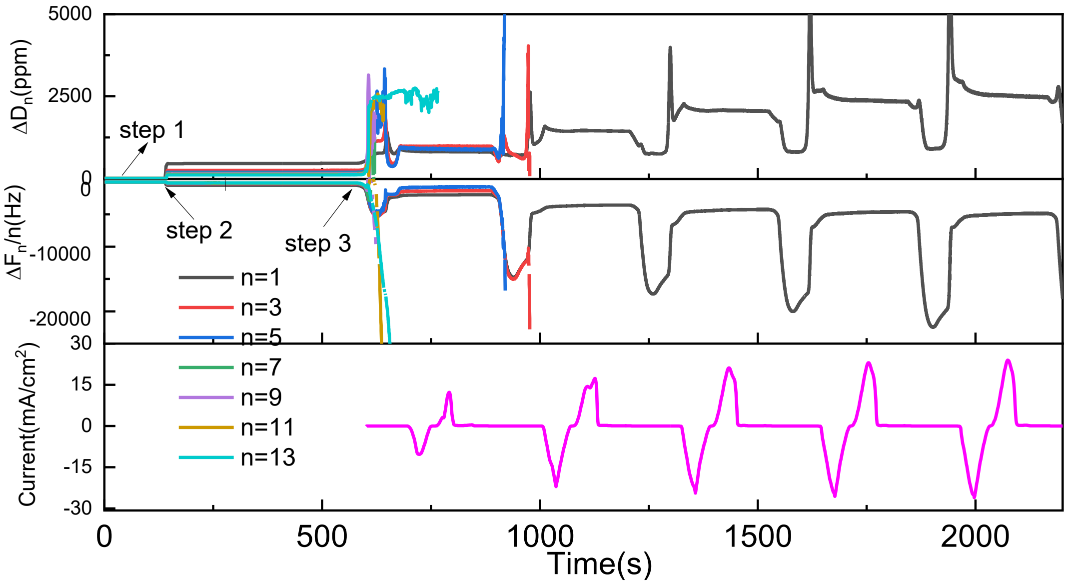

Figure S2. The raw in situ EQCM-D spectroscopy recorded during three steps. The responses from 1st to 13th overtone orders are indicated by the different color lines. The high overtones lost signals due to heavy damping occurred during the CV scans.

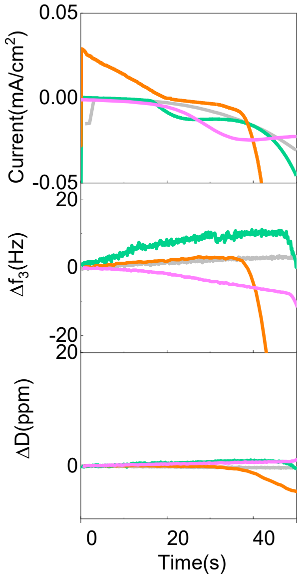

Figure S3. Enlarged view of EQCM-D spectra in the surface adsorption process.

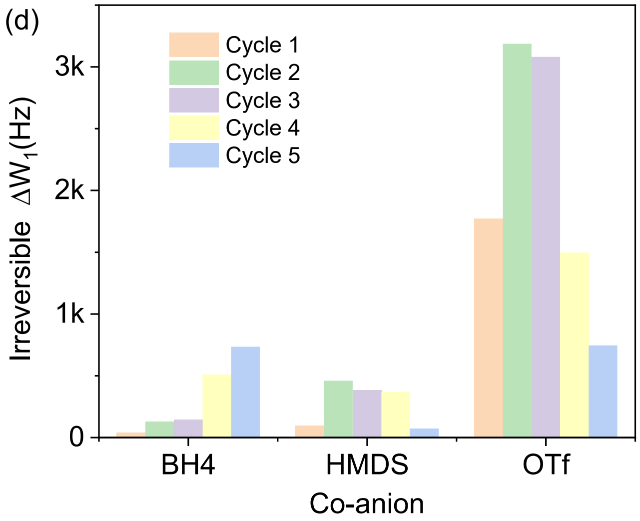

Figure S4. Irreversible change(the difference between plating and string process) in Bandwidth (ΔW) as cycle progress.

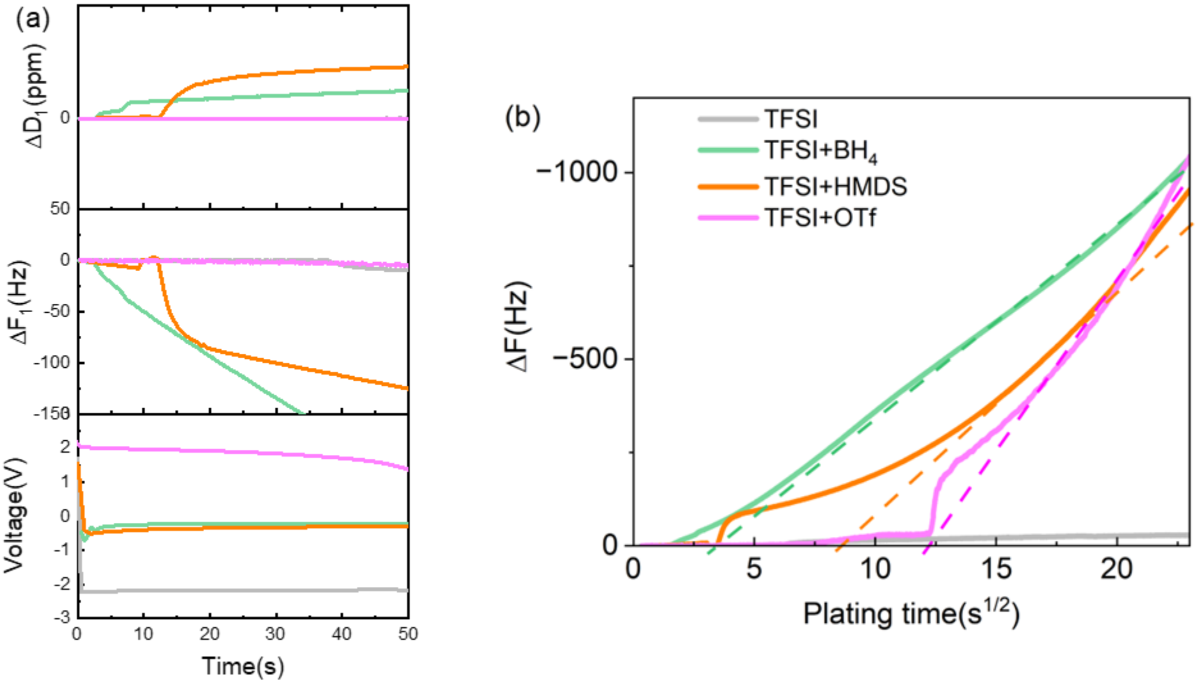

Figure S5: (a) Enlarged view of EQCM-D spectra in the CP deposition process. (b) Frequency change vs. square root of plating time.

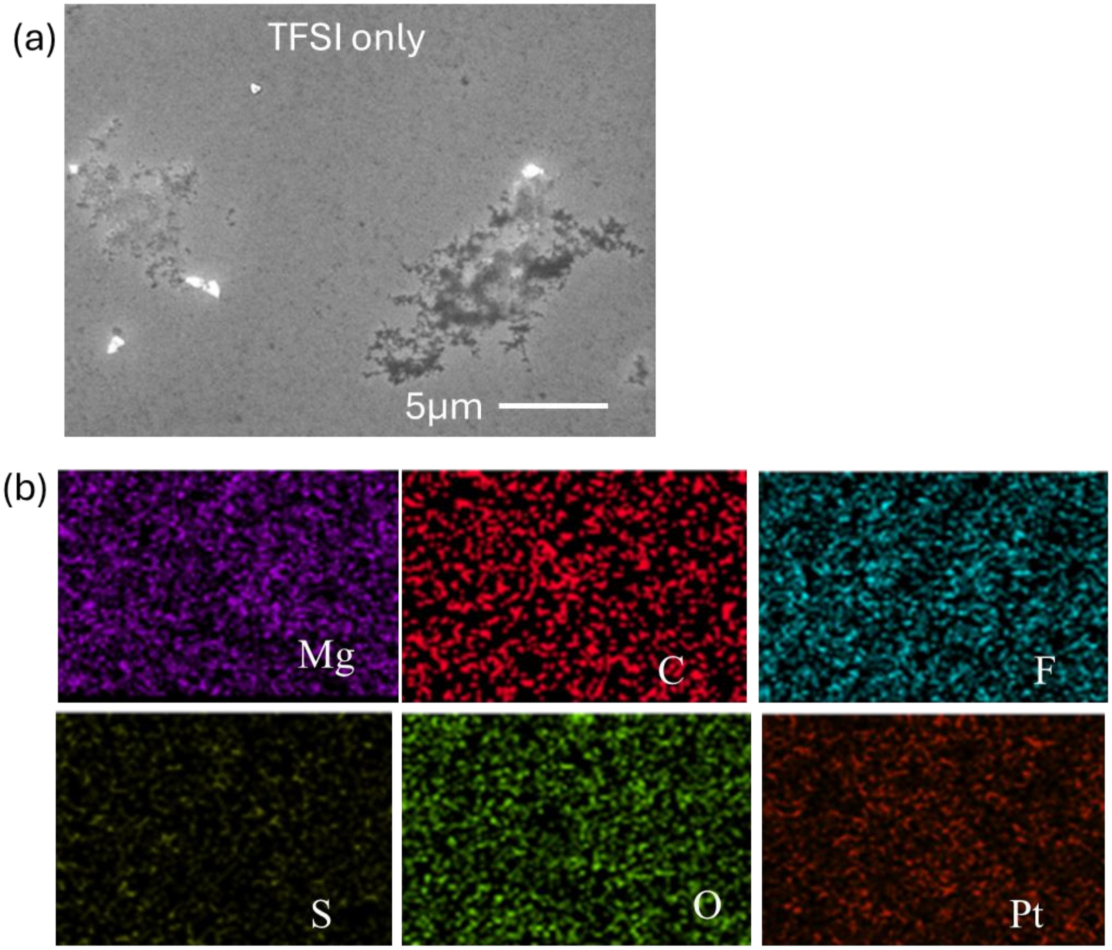

Figure S6. (a) SEM image of the Pt coated crystal electrode after CP deposition in the baseline TFSI electrolyte, showing no visibly discernible Mg deposits. (b) Representative EDS elemental maps of the deposit formed in the TFSI + BH_4 electrolyte, including Mg, C, O, F, and S. Because the deposited film is thin and the X-ray penetration depth is relatively large, signals from the underlying Pt-coated quartz crystal are also detected.