Supplementary Information (SI) for Journal of Materials Chemistry A.

Decoupling Anodic Passivation from Electrodeposition: Synergistic Crystallographic and Electronic Modulation for Energy-Efficient EMD Electrowinning

Luli Feng [a], Fengwei Xie [a], Ziyi Xu [a], Renzi Yuan [a], Linping Yu [b,*], Weijun Shen [c], Yuehui He [a,*]

[a] State Key Laboratory of Powder Metallurgy, Powder Metallurgy Research Institute, Central South University, Changsha 410083, P. R. China.

[b] Hunan Provincial Key Laboratory of Materials Protection for Electric Power and Transportation, Changsha University of Science and Technology, Changsha 410114, P. R. China.

[c] College of Mechanical Engineering, Hunan Institute of Engineering, Xiangtan 411104, China

*Corresponding author.

E-mail: linping_yu@csust.edu.cn (L.P. Yu); E-mail: yuehui@csu.edu.cn (Y.H. He)

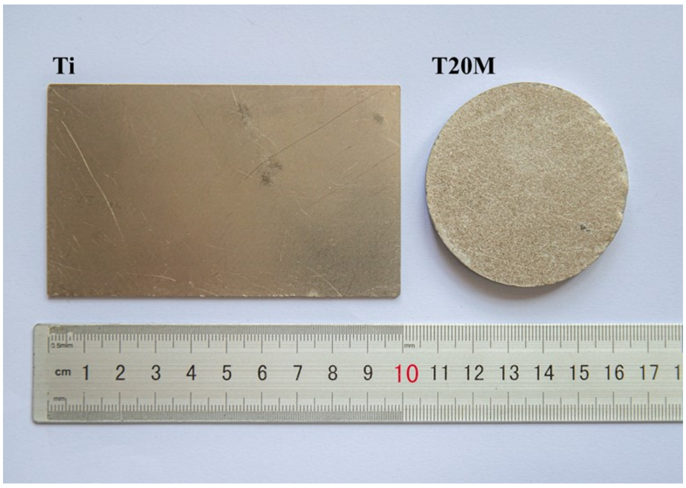

Fig. S1 Macroscopic optical photographs of the pristine pure Ti plate and the as-fabricated T20M bulk alloy.

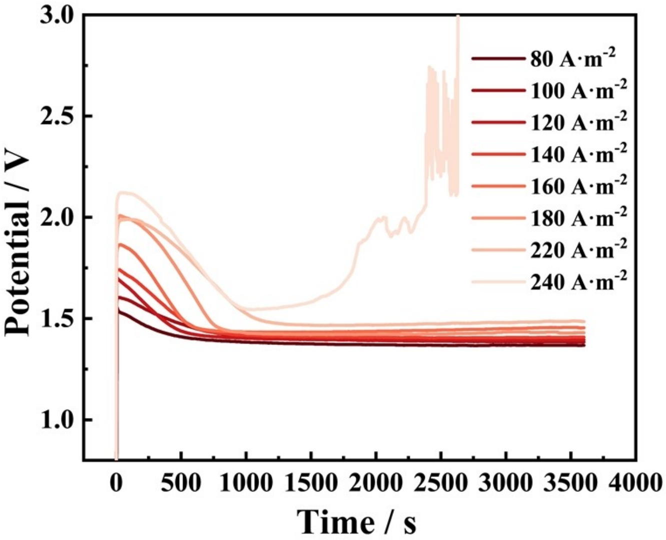

Fig. S2 Chronopotentiometry profiles of the T20Mq anode at current densities ranging from 80 to 240 A·m^{-2}

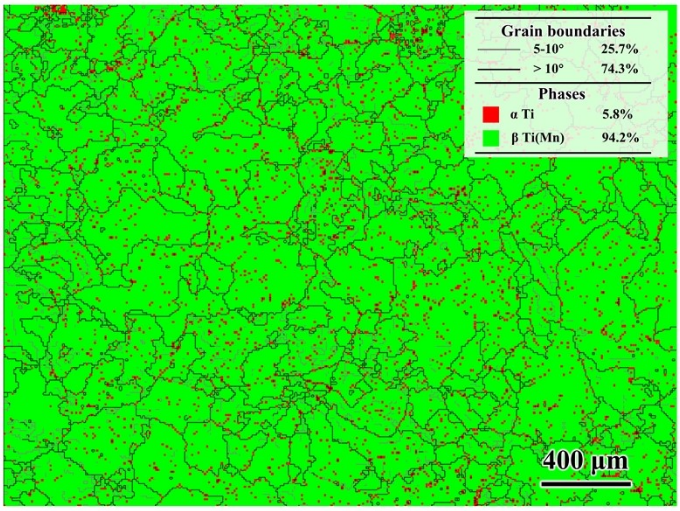

Fig. S3 The phase image corresponding to the EBSD image of T20Mq in Fig.3.

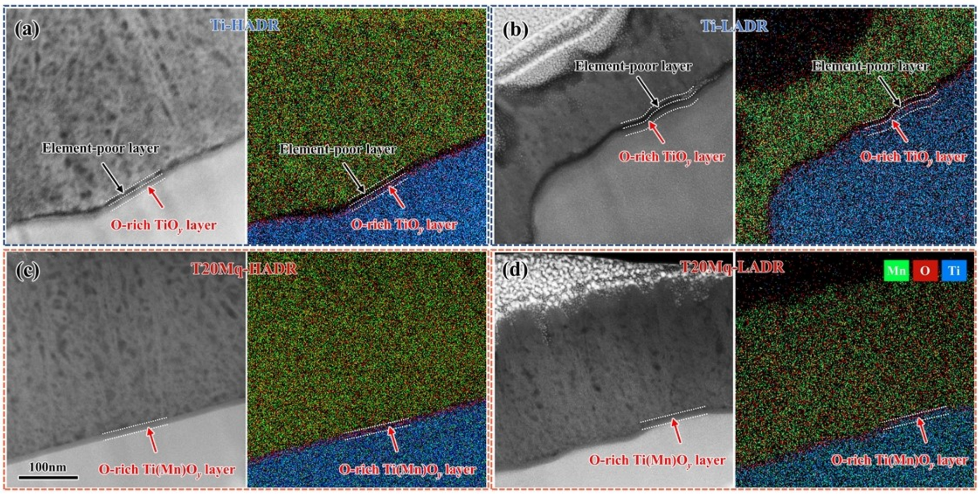

Fig. S4 STEM images and corresponding EDS elemental maps of the EMD/anode interfaces within the HADR and LADR zones. (a, b) Ti anode. (c, d) T20Mq anode.

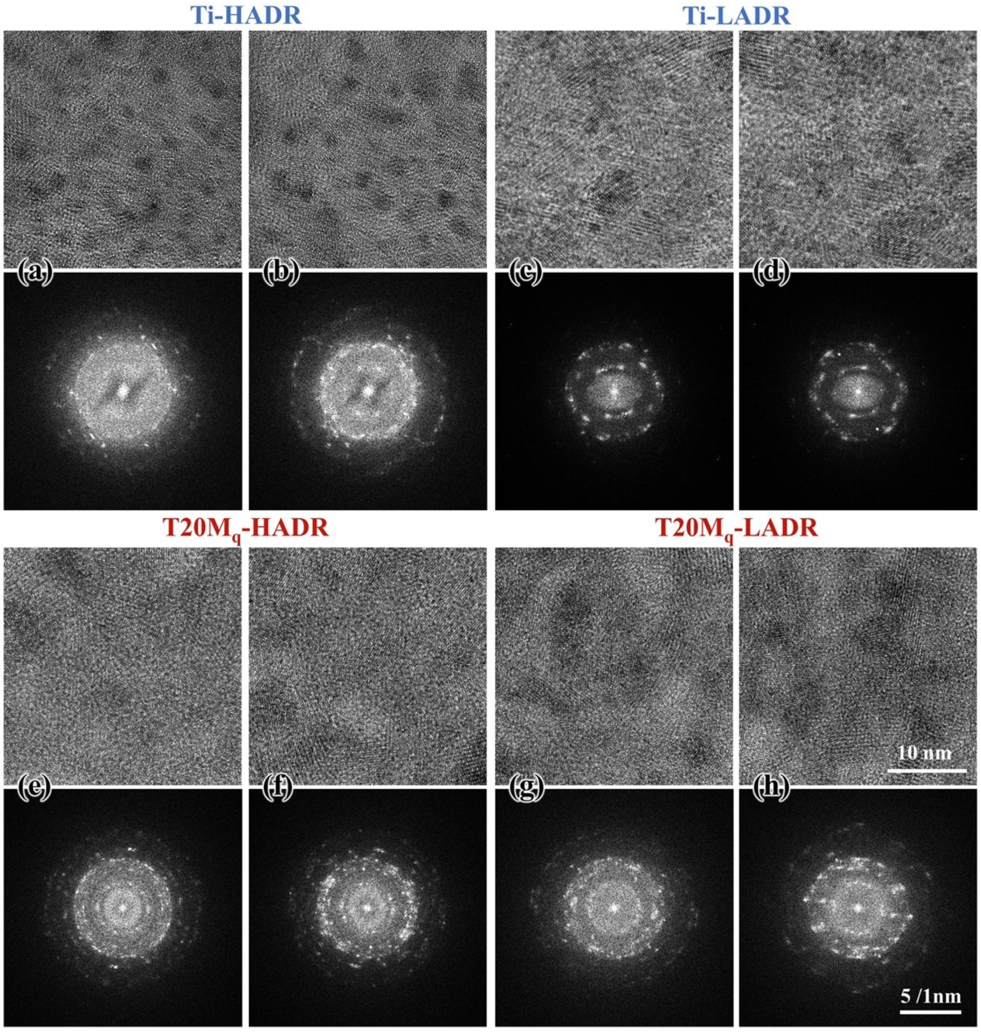

Fig. S5 HRTEM images and corresponding FFT patterns of the EMD deposit at distances of 20 nm and 80 nm from the interface. (a, b) Ti anode (HADR). (c, d) Ti anode (LADR). (e, f) T20Mq anode (HADR). (g, h) T20Mq anode (LADR).

Table S1 The corrosion potential (E_{corr}) and corrosion current (I_{corr}) corresponding to Fig. 1f

Samples	E_{corr} (V)	I_{corr} (10^{-4} A·cm^{-2})
Ti	-0.650	8.741
T20Ms	-0.731	22.91
T20Mq	-0.701	32.08

Table S2 Electrochemical impedance parameters fitted for the Ti and T20M anode

Sample	R_s (Ω)	$Y_{0,\ film}$ (10^{-4} $S\cdot s^n$)	n_{film}	R_{film} (Ω)	$Y_{0,\ dl}$ (10^{-2} $S\cdot s^n$)	n_{dl}	R_{ct} (Ω)	χ^2 (10^{-4})	Circuit Code
Ti	1.52	2.32	0.89	39.04	3.06	0.83	46.79	2.24	R(QR(QR))
T20Ms	1.08	10.5	0.81	10.31	5.69	0.80	16.22	36.7	R(QR(QR))
T20Mq	1.00	5.92	0.86	10.48	5.83	0.90	14.14	8.86	R(QR(QR))

The equivalent circuit used for fitting is $R_s(Q_{film}R_{film})(Q_{dl}R_{ct})$, where $(Q_{film}R_{film})$ represents the response of the surface oxide film, and $(Q_{dl}R_{ct})$ corresponds to the double-layer capacitance and charge transfer resistance at the electrode/electrolyte interface.

All impedance parameters are normalized to the geometric area of the electrode (1 cm^2).

Table S3. Electrochemical impedance parameters fitted for the Ti anode during electrodeposition.

Time (s)	R_s (Ω)	$Y_{0,int}$ (10^{-5} S·s^n)	n_{int}	R_{int} (Ω)	χ^2 (10^{-4})	Circuit Code
120	1.32	2.45	0.957	420.1	2.05	R(QR)
240	1.35	2.46	0.956	270.9	2.86	R(QR)
480	1.29	3.94	0.908	175.9	5.79	R(QR)
960	1.34	3.70	0.912	161.3	4.94	R(QR)
1920	1.39	3.41	0.917	172.7	3.96	R(QR)
3840	1.53	3.35	0.913	202.0	5.78	R(QR)
10800	1.95	2.97	0.909	330.6	13.6	R(QR)
36000	5.67	1.66	0.936	387.6	8.88	R(QR)
stripped	2.20	1.65	0.941	347.7	15.9	R(QR)

All impedance parameters are normalized to the geometric area of the electrode (1 cm^2).

Circuit Codes: R(QR) represents the model $R_s(Q_{int}R_{int})$, where R_{int} reflects the total interfacial resistance dominated by the passive film.

Table S4. Electrochemical impedance parameters fitted for the T20Mq anode during electrodeposition.

Time (s)	R_s (Ω)	$Y_{0,1}$ (10^{-5} S·s^n)	n_1	R_1 (Ω)	$Y_{0,2}$ (10^{-3} S·s^n)	n_2	R_2 (Ω)	W (Ω·s$^{-0.5}$)	χ^2 (10^{-4})	Circuit Code
120	1.17	4.01	0.87	-	-	-	40.58	-	54.6	R(QR)
240	1.13	10.4	0.79	-	-	-	27.45	-	32.3	R(QR)
480	1.20	45.2	0.65	-	-	-	15.19	-	16.2	R(QR)
960	1.59	4.82	0.90	2.01	1.06	0.74	4.15	-	0.54	R(QR)(QR)
1920	1.70	2.28	1.00	1.19	1.82	0.65	4.64	-	6.84	R(QR)(QR)
3840	1.77	2.19	1.00	1.25	6.50	0.51	4.90	-	6.08	R(QR)(QR)
10800	2.33	3.20	0.91	-	-	-	2.10	0.193	8.77	R(Q(RW))
36000	3.73	1.41	1.00	-	-	-	2.41	0.073	13.5	R(Q(RW))
Stripped	1.40	3.27	0.93	-	-	-	2.68	0.764	0.35	R(Q(RW))

All impedance parameters are normalized to the geometric area of the electrode (1 cm^2).

"-" indicates that the parameter is not applicable in the equivalent circuit model.

Column Definitions: Subscripts '1' and '2' denote the high-frequency and low-frequency time constants, respectively.

R_1: Resistance of the inner conductive film (R_{in}).

R_2: Primary charge transfer resistance (R_{ct}).

$Y_{0,1}$ / $Y_{0,2}$: CPE magnitude for the inner interface (CPE_{in}) and outer porous layer (CPE_{out}), respectively.

Circuit Codes: R(QR) represents the model $R_s(Q_{int}R_{int})$ for nucleation; R(QR)(QR) represents $R_s(Q_{in}R_{in})(Q_{out}R_{ct})$ for bi-layer growth; R(Q(RW)) represents $R_s(Q_{in}(R_{ct}W))$ for diffusion-controlled steady state.

Table S5 Calculated electrochemically active surface area (ECSA) and roughness factor (R_f).

Time (s)	Ti			T20Mq		
	$Y_{0,int}$ (10^{-5} S·s^n)	ECSA (cm^2)	Rf	Y_0 (10^{-5} S·s^n)	ECSA (cm^2)	Rf
120	2.45	0.61	0.61	4.01	1.00	1.00
240	2.46	0.62	0.62	10.4	2.60	2.60
480	3.94	0.98	0.98	45.2	11.30	11.30
960	3.70	0.93	0.93	106	26.50	26.50
1920	3.41	0.85	0.85	182	45.50	45.50
3840	3.35	0.84	0.84	650	162.50	162.50
10800	2.97	0.74	0.74	-	-	-

The electrochemically active surface area (ECSA) was calculated based on the double-layer capacitance (C_{dl}) derived from EIS. The calculation follows the standard relationship:

$$R_f = \frac{C_{dl}}{c_S}$$

$$ECSA = R_f \cdot A_{geo}$$

Where:

C_{dl} is the measured double-layer capacitance (approximated by the CPE magnitude Y_0 in S·s^n·cm^{-2}, normalized to geometric area).

Cs is the specific capacitance of a smooth standard surface, taken as 40 μF·cm^{-2}.

R_f is the roughness factor, representing the ratio of real active area to geometric area.

A_{geo} is the geometric surface area of the electrode. In this work, A_{geo} = 1.0 cm^2, thus the numerical value of ECSA (cm^2) is identical to R_f.

For the T20Mq anode at steady state (>10800 s), the ECSA calculation is not applicable because the low-frequency capacitive response of the porous layer is dominated by the diffusion process.