Carbides of group IVA, VA and VIA transition metals as alternative HER and ORR catalysts and support materials

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Supplementary Information

Table S1: Eutectic salt flux composition, annealing temperatures and annealing times for the synthesis of TMCs.

M_xC_y	Molar ratio of salts	Annealing temperature (°C)	Annealing time (hr)
TiC	*LiCl:KCl:KF = 58:40:2*	960	5
V_8C_7	*LiCl:KCl:KF = 58:40:2*	950	12
Cr_3C_2	*LiCl:KCl:KF = 58:40:2*	950	12
ZrC	*LiCl:KCl:KF = 58:40:2*	950	12
Nb_4C_3	*LiCl:KCl:KF = 58:40:2*	950	12
Mo_2C	*LiCl:KCl:KF = 58:40:2*	950	12
HfC	*LiCl:KCl:KF =58:40:2*	750	5
TaC	*LiCl:KCl:KF =58:40:2*	950	12
WC	*NaF:NaCl = 7:10*	1050	36

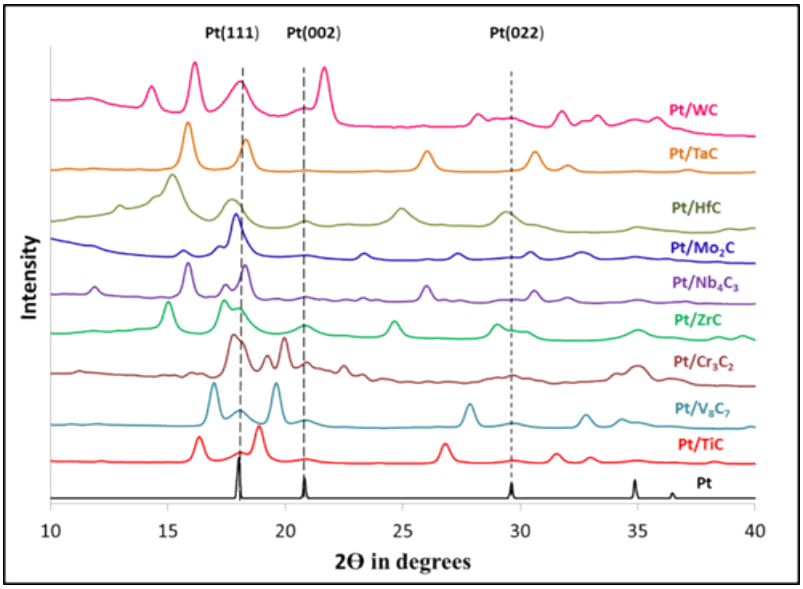

Figure S1: XRD patterns of Pt/TMCs. The dashed lines indicate the three major diffraction peaks for Pt (PDF # 01-087-0640).

Table S2: BET surface area of MCs using N_2 as the adsorbent gas. MWCNT is the commercially available multiwalled carbon nanotubes.

M_xC_y	A (m^2/g)
TiC	12.00 ± 0.21
V_8C_7	7.16 ± 0.03
Cr_3C_2	18.53 ± 0.16
ZrC	40.73 ± 0.20
Nb_4C_3	10.07 ± 0.71
Mo_2C	31.32 ± 0.12
HfC	28.80 ± 0.12
TaC	29.01 ± 0.07
WC	38.54 ± 2.26
MWCNT	234.36 ± 1.00

Table S3: Concentration of Pt determined from ICP-OES. Three most intense wavelengths were used to measure the concentration. No interference was observed in any of the three wavelengths used in the measurements.

M_xC_y	PPM Pt	% Pt loading
TiC	8.001	9.690
V_8C_7	10.371	12.560
Cr_3C_2	10.163	12.307
ZrC	7.015	8.495
Nb_4C_3	7.751	9.387
Mo_2C	5.956	7.212
HfC	9.601	11.627
TaC	9.119	11.044
WC	5.333	6.458

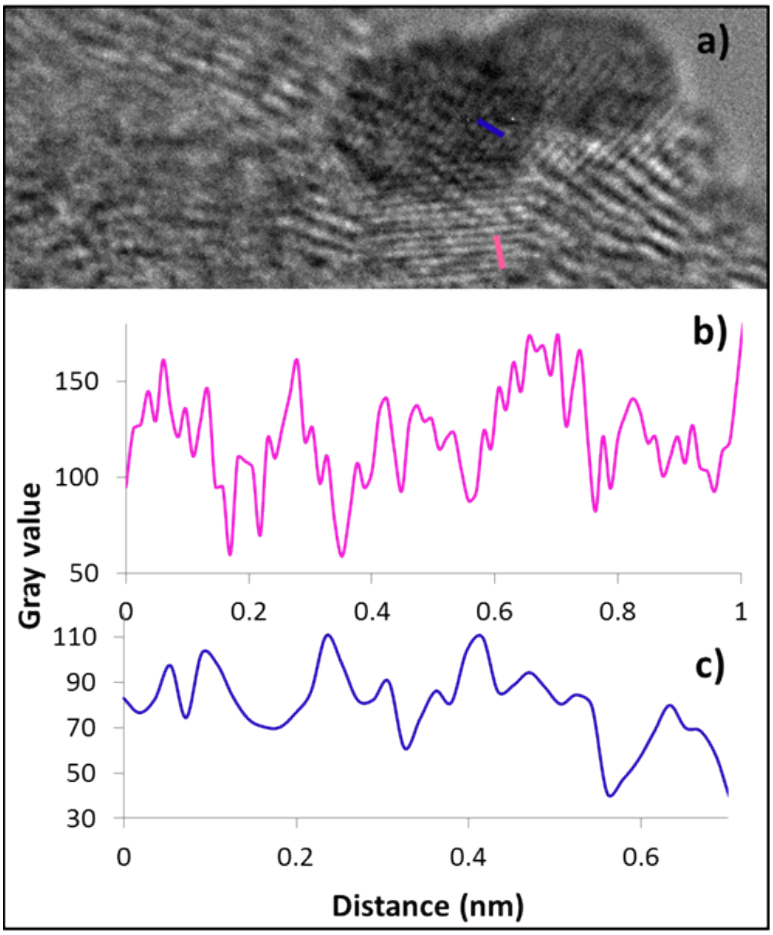

Figure S2: Line profile for TEM micrographs of Pt/WC. a) TEM micrograph of Pt/WC with fringe patterns for WC (light areas) and Pt (dark areas). b) Line profile of WC c) Line profile of Pt

Tabel S4: D-spacing for lattice planes of Pt, WC and multiwalled carbon nanotubes (MWCNT)

Lattice plain	D-spacing (nm)
Pt (111)	0.226
Pt (002)	0.196
Pt (022)	0.139
Pt (113)	0.118
WC (001)	0.284
WC (010)	0.252
WC (011)	0.188
WC (110)	0.145
WC (111)	0.129
WC (012)	0.124
WC (021)	0.115
WC (112)	0.102
MWCNT (002)	0.335
MWCNT (011)	0.203

Equation S1

$$\text{Potential (V)}_{\text{RHE}} = \text{Potential (V)}_{\text{Ag/AgCl}} + 0.197 + \text{pH}*0.059$$

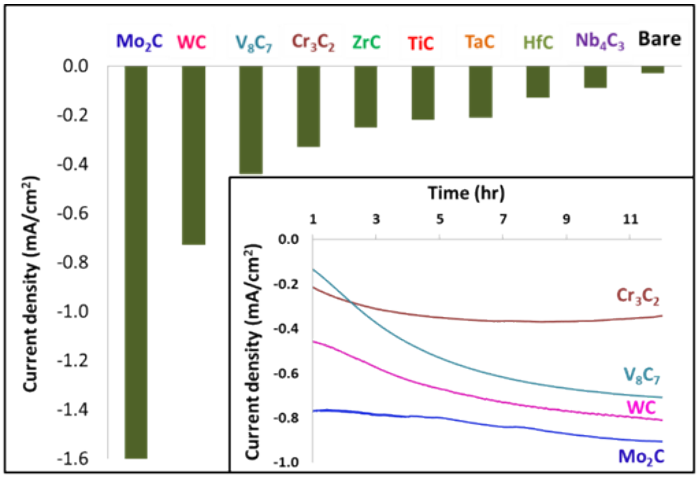

Figure S3: HER current density of TMCs at -344 mV vs RHE measured at 2 mV/s and 2500 rpm in 0.1 M $HClO_4$. Bare is unmodified glassy carbon electrode. The inset represents the controlled potential electrolysis plot for Mo_2C, WC, V_8C_7 and Cr_3C_2 recorded at -294 mV vs RHE, for 12 hours.

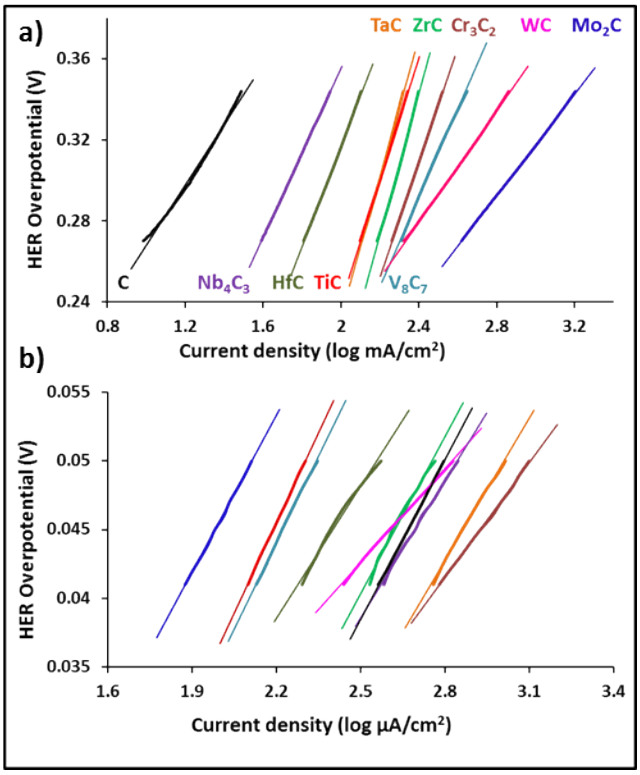

Figure S4: Tafel plots of HER polarization curves for a) TMCs in figure 4 and b) Pt/TMCs from figure 6. The best fit lines are included for each system. Ohmic drop correction was not applied to the polarization data.

Table S5: Tafel slopes and exchange current densities for TMCs and Pt/TMCs based on figure S4. Tafel slopes and exchange currents were generated by fitting the data to the Tafel equation $\eta = b \log(\mathbf{j}) + a$ where η is the overpotential, b is the tafel slope, **j** is the current density corresponding to the overpotentials and a is the y-intercept. The exchange current densities were calculated when $\eta = 0$ V. Ohmic drop corrections were not applied.

	carbide		Pt/carbide	
	Tafel slope *mV/decade*	Exchange current *µA/cm²*	Tafel slope *mV/decade*	Exchange current *µA/cm²*
Mo_2C	124.8	2.86	38.0	6.27
WC	137.1	2.30	22.7	4.27
TaC	345.9	21.32	34.7	1.44
Nb_4C_3	209.4	2.01	33.4	22.10
Cr_3C_2	283.7	20.43	27.8	20.22
C	NA	NA	38.7	32.10
ZrC	350.6	26.43	37.9	27.25
HfC	250.0	5.40	31.9	9.93
V_8C_7	218.9	11.65	41.8	14.00
TiC	301.4	15.97	43.7	14.46

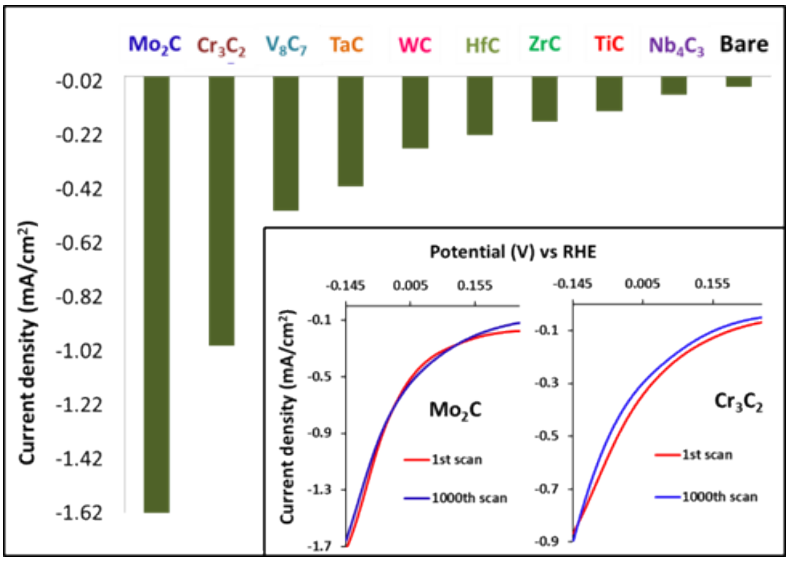

Figure S5: ORR current density of TMCs at -144 mV vs RHE measured at 50 mV/s and 1600 rpm in 0.1 M $HClO_4$. Bare is unmodified glassy carbon electrode. The inset represents the LSV curves for 1st and 1000th cycles for Mo_2C and Cr_3C_2.

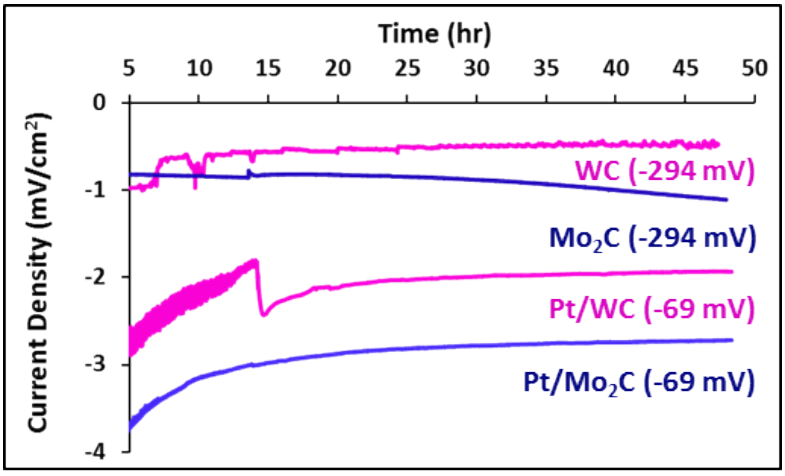

Figure S6: HER current densities from controlled potential indicated electrolysis at various applied potentials vs RHE for Mo_2C, Pt/Mo_2C , WC and Pt/WC for 48 hours at 2500 rpm in 0.1 M $HClO_4$.

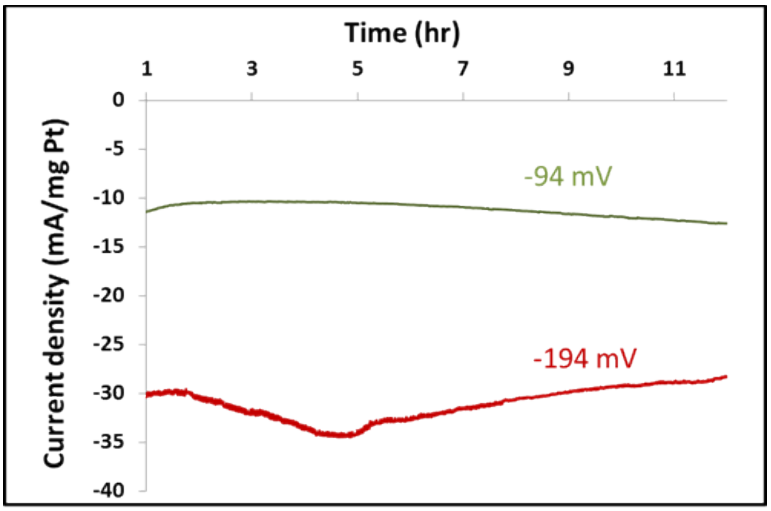

Figure S7: HER current normalized to Pt loading from controlled potential electrolysis at -94 and -194 mV applied potentials for Pt/TiC for 12 hours at 2500 rpm in 0.1 M $HClO_4$.