Electronic Supplementary Information†

Low-cost industrially available molybdenum boride and carbide as "platinum-like" catalysts for the hydrogen evolution reaction in biphasic liquid systems

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Table S1. Calculated equilibrium concentrations (mM) of each of the constituent ions for the shake-flask outlined in Scheme 1, main text, (aqueous phase of 100 mM HCl; organic phase of 10 mM LiTB and 2.5 mM DMFc in 1,2-DCE) for the initial partition of the electrolyte ions and at a time (t = x) when full conversion of DMFc to DMFc$^+$ (and concomitant consumption of protons) has taken place.[A]

Partitioning ion	$\Delta G_{tr,i}^{0,o \to w}$ (kJ·mol^{-1})	$\Delta_o^w \phi_{tr,i}^0$ V	Aqueous Initial	1,2-DCE Initial	Aqueous (t = x)	1,2-DCE (t = x)
[H$^+$]$_{eq}$ / mM	-56.0	0.58	90.11	9.89	90.08	7.42
[Li$^+$]$_{eq}$ / mM	-62.7	0.64	9.89	0.11	9.92	0.079
[TB$^-$]$_{eq}$ / mM	68.5	0.71	0.007	9.993	0.005	9.995
[Cl$^-$]$_{eq}$ / mM	-51.1	-0.53	100	1.569×10^{-16}	100	2.092×10^{-16}
[DMFc$^+$]$_{eq}$ / mM	25.1	-0.26	-	-	3.945×10^{-10}	2.5

[A] The Galvani potential difference ($\Delta_o^w \phi$) is calculated as 0.523 V for the initial partition of the electrolyte ions and 0.516 V at a time when full conversion of DMFc to DMFc$^+$ has taken place. The Gibbs energy of transfer ($\Delta G_{tr,i}^{0,o \to w}$), and consequently the standard ion transfer potential ($\Delta G_{tr,i}^{0,o \to w} = -z_i F \Delta \phi_{tr,i}^{0,o \to w}$), for each electrolyte ion and DMFc$^+$ were obtained from references (s1) and (s2), respectively.

Optimisation of the quantities of catalytic microparticles required for biphasic HER kinetics studies
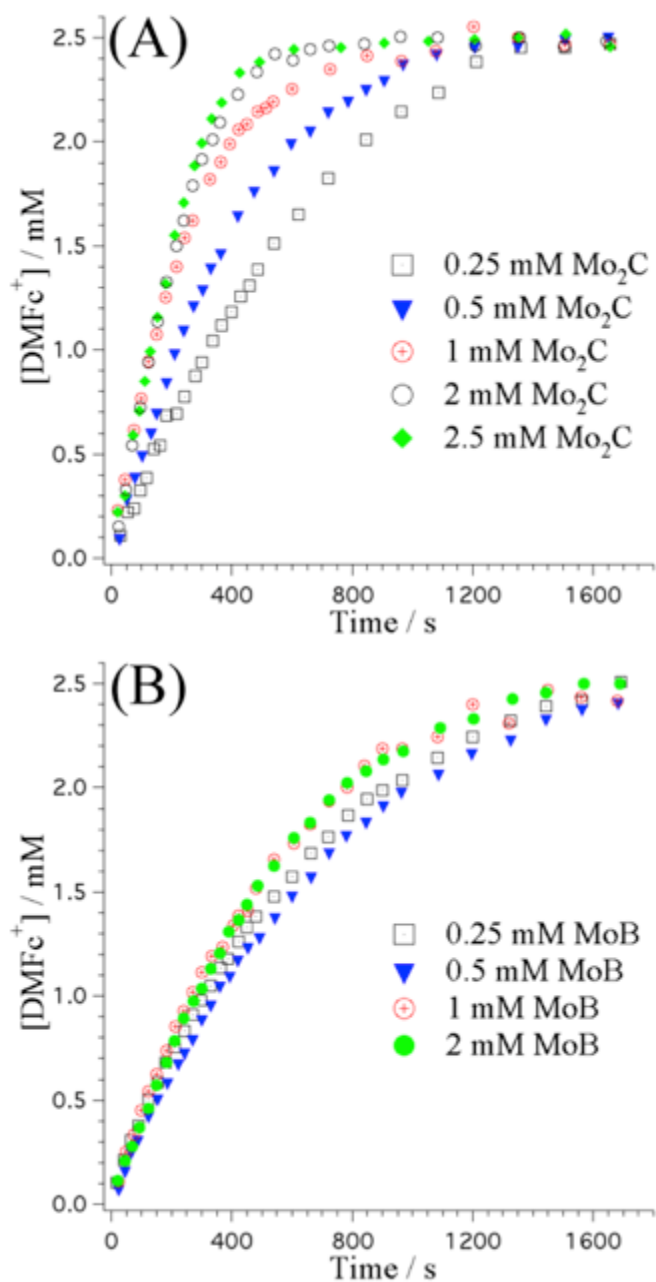
Fig. S1. Optimisation of the quantity of catalyst required for observation of the maximum biphasic HER rates for **(A)** Mo_2C and **(B)** MoB. The kinetics of the biphasic HER with chemically controlled polarization, see Scheme 1, for each concentration of catalyst were followed by monitoring changes in the UV/Vis absorbance ($\lambda_{max} = 779$ nm) of organic solublised $DMFc^+$.

Determination of the reaction order with respect to proton concentration for biphasic

reactions in the presence of each catalytic microparticle

The rate of reaction for the catalyzed biphasic HER by can be written as

$$v = k \left[\text{DMFc} \right]^a \left[\text{H}^+ \right]^b \qquad \text{(S1)}$$

where a and b are the reaction orders for [DMFc] and [H$^+$], respectively. The rate of reaction with respect to [DMFc] was found to be first order in the presence of Mo_2C and MoB microparticles and zero order with Pt, W_2C and WC microparticles present (Fig. 5(A), main text). Thus, to determine the reaction order with respect to protons for Mo_2C and MoB microparticles the logarithm of the rate of reaction is

$$\ln(v) - \ln\left(\left[\text{DMFc}\right]\right) = \ln(k) + b\ln\left(\left[\text{H}^+\right]\right) \qquad \text{(S2)}$$

whereas, for Pt, W_2C and WC microparticles the logarithm of the rate of reaction reads

$$\ln(v) = \ln(k) + b\ln\left(\left[\text{H}^+\right]\right) \qquad \text{(S3)}$$

Thus, the reaction order with respect to proton concentration (b) for each catalytic microparticle was determined by plotting $\ln(v)$-$\ln([\text{DMFc}])$ *vs.* $\ln([\text{H}^+])$ for Mo_2C and MoB microparticles and by plotting $\ln(v)$ *vs.* $\ln([\text{H}^+])$ for Pt, W_2C and WC microparticles. Zero order kinetics with respect to proton concentration for each catalyst was observed, see Fig. S2.
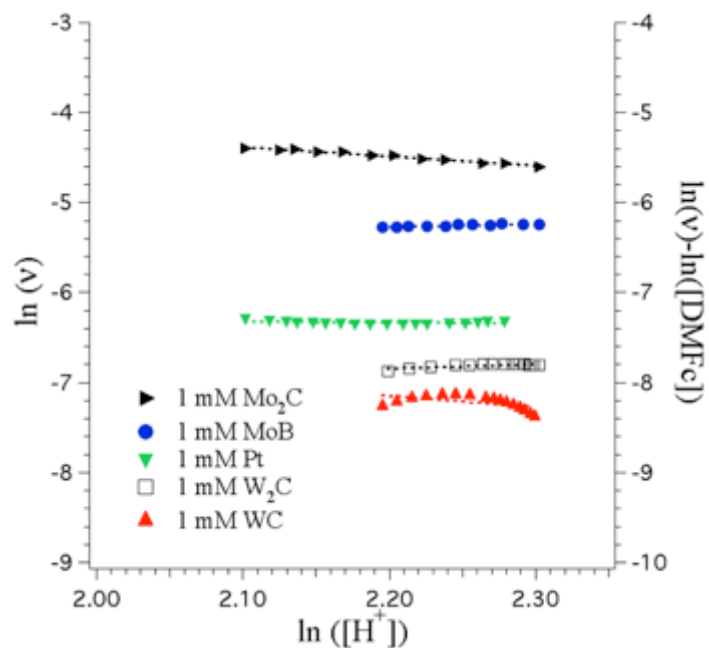
Fig. S2. *Rate order determination with respect to protons*: For Pt, W_2C and WC the natural logarithm of the reaction rate, ln (ν), estimated from the slope of the polynomial fit to the experimental data, was plotted as a function of the natural logarithm of proton concentration, ln ($[H^+]$). For Mo_2C and MoB, ln (ν)-ln ($[DMFc]$) was plotted as a function ln ($[H^+]$).

Cyclic voltammetry control experiments
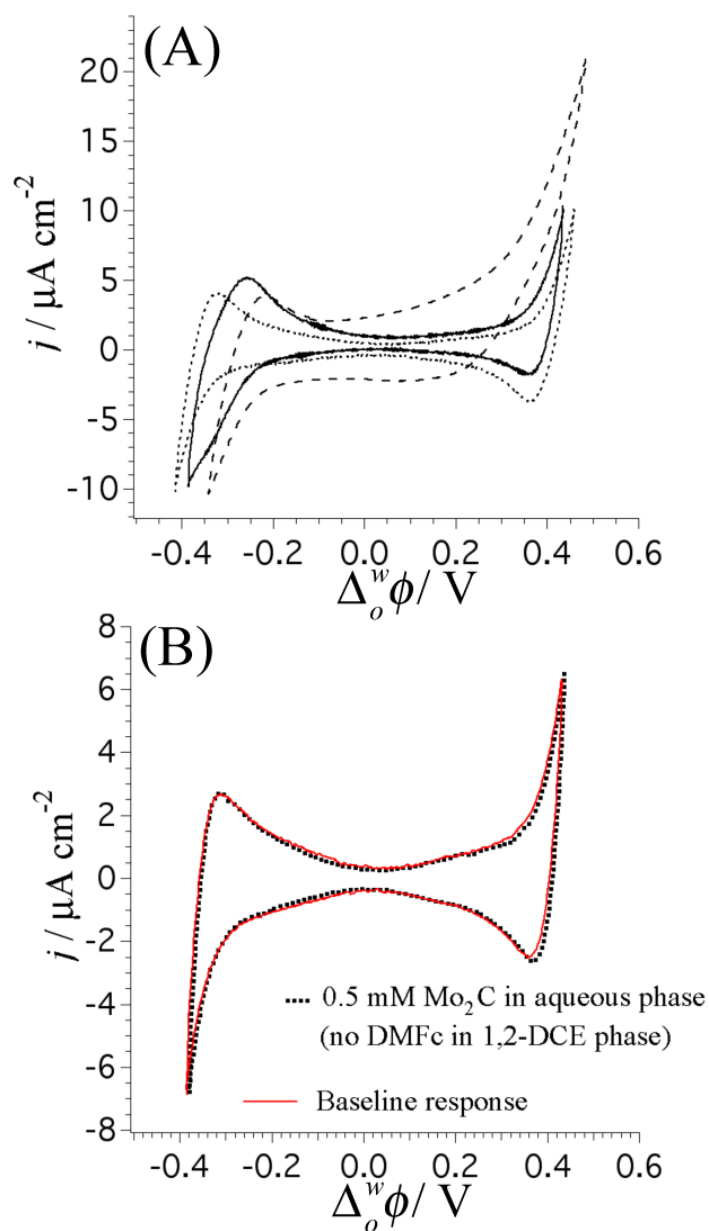
Fig. S3. Cyclic voltammograms for electrochemical cells (see Scheme 2, main text) comparing the baseline response (x = 0, y = 0, z = 5; dotted line) to that (A) in the presence of organic solubilised DMFc but absence of Mo_2C (x = 2.5, y = 0, z = 5; solid line), in the presence of both Mo_2C and organic solubilised DMFc (x = 2.5, y = 0.5, z = 5; dashed line) and (B) in the presence of Mo_2C but absence of organic solubilised DMFc (x = 0, y = 0.5, z = 5; red solid line). Scan rate: 50 mV s^{-1}.

Derivation of the Nernst equation for the biphasic hydrogen evolution reaction

The global reaction for biphasic hydrogen evolution reads

$$DMFc^o + H^{+,w} \xrightarrow{\ catalyst\ } DMFc^{+,o} + \frac{1}{2}H_2 \qquad (S4)$$
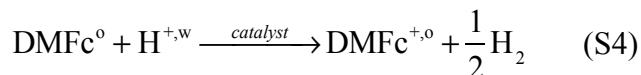
where w and o denote the aqueous and organic phases, respectively. From a thermodynamic viewpoint, the work required to transfer a mole of ions, such as $DMFc^+$ or protons, from a vacuum to a liquid phase, α (i.e. w or o), is defined as the electrochemical potential, $\tilde{\mu}_i^\alpha$, where

$$\tilde{\mu}_i^\alpha = \mu_i^\alpha + z_i F \phi^\alpha \qquad (S5)$$

The $z_i F \phi^\alpha$ term is the electrical work required to transfer the charge that the ion possesses into phase α. An ion in solution will have short-distance interactions with its environment, for example ion-dipole interactions, dispersion forces, and hydration to some extent will occur. Thus, the energy level of the ion in a phase clearly depends on its chemical environment. This is represented by μ_i^α, the chemical potential of ion i in phase α. For an uncharged species, such as DMFc, the electrochemical potential is solely dependent on this chemical contribution such that $\tilde{\mu}_i^\alpha = \mu_i^\alpha$. In solution, μ_i^α is represented by

$$\mu_i^\alpha = \mu_i^{\alpha,0} + RT \ln a_i^\alpha \qquad (S6)$$

where $\mu_i^{\alpha,0}$ is the standard chemical potential and a_i^α is the activity of the ion i. The activity is a measure of the effective concentration of species i in solution. Activity depends on temperature, pressure and composition of the solution, among other factors.

For a real gas, such as H_2, the chemical potential for a given pressure may be expressed with regard to a standard pressure value, p^0, of 1 bar as[s3]

$$\mu_i^\alpha = \mu_i^{\alpha,0} + RT \ln\left(\frac{f}{p^0}\right) \qquad (S7)$$

where f is the fugacity, a term that takes into account the partial pressure of the real gas and deviations of its behaviour with respect to an ideal gas.

When an electrochemical cell is balanced against an external source of potential, and the entire system is at equilibrium, then the Gibbs energy (ΔG) for a reaction is zero and

$$\Delta G = \sum\nolimits_{\text{Products}} n_i \Delta G_i - \sum\nolimits_{\text{Reactants}} n_j \Delta G_j = 0 \qquad \text{(S8)}$$

where n_i and n_j and the stoichiometric coefficients for the product and reactant species, respectively. Thus, the Gibbs energy of the PCET reaction outlined in eqn (S4) at equilibrium can be expressed in terms of the electrochemical potentials of each of the reactant and product species and is

$$\Delta G = \tilde{\mu}^{\text{o}}_{\text{DMFc}^+} + \frac{1}{2}\tilde{\mu}_{\text{H}_2} - \left[\tilde{\mu}^{\text{o}}_{\text{DMFc}} + \tilde{\mu}^{\text{w}}_{\text{H}^+} \right] = 0 \quad \text{(S9)}$$

In turn, eqn (S9) leads directly to

$$\Delta G = \mu^{0,\text{o}}_{\text{DMFc}^+} + RT\ln a^{\text{o}}_{\text{DMFc}^+} + z_{\text{DMFc}^+} F\phi^{\text{o}} + \frac{1}{2}\mu^{0}_{\text{H}_2} + RT\ln\left(\frac{f_{\text{H}_2}^{1/2}}{p^0} \right) - $$
$$\left[\mu^{0,\text{o}}_{\text{DMFc}} + RT\ln a^{\text{o}}_{\text{DMFc}} + \mu^{0,\text{w}}_{\text{H}^+} + RT\ln a^{\text{w}}_{\text{H}^+} + z_{\text{H}^+} F\phi^{\text{w}} \right] = 0 \qquad \text{(S10)}$$

Rearranging eqn (S10) we get

$$\Delta G = (\mu^{0,\text{o}}_{\text{DMFc}^+} - \mu^{0,\text{o}}_{\text{DMFc}}) + (\frac{1}{2}\mu^{0}_{\text{H}_2} - \mu^{0,\text{w}}_{\text{H}^+}) + RT\ln\left(\frac{a^{\text{o}}_{\text{DMFc}^+}}{a^{\text{o}}_{\text{DMFc}} a^{\text{w}}_{\text{H}^+}} \right)\left(\frac{f_{\text{H}_2}^{1/2}}{p^0} \right) + z_{\text{DMFc}^+} F\phi^{\text{o}} - z_{\text{H}^+} F\phi^{\text{w}} = 0 \quad \text{(S11)}$$

The following factors are taken into consideration:

(1) $z_{\text{DMFc}^+} = z_{\text{H}^+} = 1,$

(2) $(\mu^{0,\text{o}}_{\text{DMFc}^+} - \mu^{0,\text{o}}_{\text{DMFc}}) + (\frac{1}{2}\mu^{0}_{\text{H}_2} - \mu^{0,\text{w}}_{\text{H}^+}) = \left[E^{0}_{\text{DMFc}^+/\text{DMFc}} \right]^{\text{o}}_{\text{SHE}}$ *i.e.* the standard redox potential of the

DMFc$^+$/DMFc couple in 1,2-DCE with respect to the aqueous standard hydrogen electrode (SHE),

(3) $RT\ln\left(\frac{a^{\text{o}}_{\text{DMFc}^+}}{a^{\text{o}}_{\text{DMFc}} a^{\text{w}}_{\text{H}^+}} \right)\left(\frac{f_{\text{H}_2}^{1/2}}{p^0} \right) = RT\ln\left(\frac{a^{\text{o}}_{\text{DMFc}^+}}{a^{\text{o}}_{\text{DMFc}}} \right) + \frac{1}{2}RT\ln\left(\frac{f_{\text{H}_2}}{p^0} \right) - RT\ln\left(a^{\text{w}}_{\text{H}^+} \right)$

At atmospheric pressure and under bubbling conditions we may neglect the term $\frac{1}{2}RT\ln\left(\frac{f_{H_2}}{p^0}\right)$ and,

additionally, $-\dfrac{RT\ln\left(a_{H^+}^w\right)}{\ln 10} = -RTLog\left(a_{H^+}^w\right) = RT\text{pH}$, therefore $-RT\ln\left(a_{H^+}^w\right) = \ln 10\, RT\text{pH}$.

Thus, re-arranging with the above factors taken into account and subsequently dividing each term by Faraday's constant yields

$$\phi^w - \phi^o = \frac{\left[E^0_{DMFc+/DMFc}\right]^o_{SHE}}{F} + \frac{RT}{F}\ln\left(\frac{a^o_{DMFc^+}}{a^o_{DMFc}}\right) + \frac{RT}{F}\ln 10\,\text{pH} \quad (S12)$$

Finally, the Nernst equation for the biphasic hydrogen evolution reaction reads

$$\Delta^w_o\phi_{HER} = \Delta^w_o\phi^0_{HER} + \frac{RT}{F}\ln\left(\frac{a^o_{DMFc^+}}{a^o_{DMFc}}\right) + \frac{RT}{F}\ln 10\,\text{pH} \qquad (S13)$$

where $\Delta^w_o\phi^0_{HER} = \dfrac{\left[E^0_{DMFc+/DMFc}\right]^o_{SHE}}{F}$ and $\Delta^w_o\phi_{HER} = \phi^w - \phi^o$, termed the redox Galvani potential difference of the hydrogen evolution reaction.

References

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(s3)   H. H. Girault, *Analytical and Physical Electrochemistry*, EPFL Press: Lausanne, Switzerland, 2004.