Polyaromatic-terminated iron(II) clathrochelates as electrocatalysts for efficient hydrogen production in water electrolysis cells with polymer electrolyte membrane

Artem S. Pushkarev, Irina V. Pushkareva, Maksim A. Solovyev, Sergey A. Grigoriev, Yan Z. Voloshin, Nina V. Chornenka, Alexander S. Belov, Pierre Millet, Manuel Antuch, Valery N. Kalinichenko and Alexey G. Dedov

Electrodes preparation and PEM water electrolysis cells assembling

CP Sigracet 39 BC (SGL Group) was used. Clathrochelates [S1–S3] **1**–**3** were physisorbed *via* a soaking of CP disks (7 cm^2) in their acetonitrile solutions. Their weight loadings on each of these disks, were slightly different due to their different adsorption capacities and molecular weights, but their surface molar concentrations were quite similar (0.164, 0.165 and 0.159 μmol.cm^{-2}, respectively) [S4, S5].

Ir black catalyst, obtained by chemical reduction of $H_2IrCl_6–6H_2O$ with $NaBH_4$ as described [S6], was used as the oxygen evolution reaction (OER) electrocatalyst at the PEM electrolysis cell anode. Circular porous titanium disks were used as GDE on the anode side [S7].

Catalytic inks were prepared as described elsewhere [S8]. An ionomer content of 5 wt.% (for Ir black) and 15 wt.% (for Pt/Vulcan XC-72) was used (% are expressed on a dry basis). The anodic (Ir black) and cathodic (Pt-containing) catalytic layers were deposited directly onto a surface of titanium GDEs [S9] by air spraying forming the anodes and the reference Pt-based cathode. Exact Pt and Ir contents were determined gravimetrically: loadings of *ca.* 2 and 1 mg cm^{-2} were obtained for Ir and Pt/Vulcan XC-72 catalysts, respectively.

Nafion® 117 (DuPont de Nemours, USA) membranes were sandwiched between the two electrocatalyst-containing GDEs, to form a membrane – electrode assembly (MEA), which was then placed in a Lab-made titanium PEM electrolysis cell [S10,S11]. The cell was then firmly

tightened, filled with deionized water and heated at 90°C. This cell consisted of two thermostatic Lab-made half-cells with integrated flow-field and a working surface area of *ca.* 7 cm^2 [S12]. All the experiments were performed at 80°C: deionised and thermostated water was continuously pumped through the anode cell compartment. To perform the experiments, an uncoated titanium disk was placed between the cathodic endplate (against a flow field) and the clathrochelate-containing electrodes or the CP-Pt/C GDEs as described in detail elsewhere [S7]. GDEs containing carbon-supported platinum nanoparticles (Pt/Vulcan XC–72 with 40 wt.% of Pt) were used as a reference.

Model i–V curves

Experimental cell polarization curves (the plots of the cell voltage U_{cell} *vs.* the operating current density *j*, at the temperature *T* and under the pressure *P*), also called i–V curves, can be fitted using the model Eq. (1), in which the different cell voltage contributions were added [S13]:

$$U_{cell}(T,P) = V(T,P) + \eta_{H_2}(T,P) + j \sum_k R_k + \eta_{O_2}(T,P) \tag{1}$$

In Eq. (1), the mass transport limitations are neglected. *V(V,P) = ΔH(T,P)/2F* is the thermoneutral water-splitting voltage at T,P (it is used instead of the Gibbs free-energy voltage E(T,P) = ΔG(T,P) because the heat demand for the entropy increase (T.ΔS) is produced internally by ohmic losses); the R_k's are the resistances of the different components of the PEM water electrolysis cell; $\eta_{O_2}(T,P)$ and $\eta_{H_2}(T,P)$ are the OER and HER overvoltages at (T,P), respectively. They are calculated using the general forms of the Butler–Volmer equations, which are valid for the multistep overall electrode reactions [S14]:

$$j_{OER}(T,P) = j^0_{OER}(T,P) \left\{ exp\left(\frac{\overleftarrow{\alpha} F}{R T} \eta_{OER}(T,P)\right) - exp\left(\frac{\overrightarrow{\alpha} F}{R T} \eta_{OER}(T,P)\right) \right\} \tag{2}$$

$$j_{HER}(T,P) = j^0_{HER}(T,P) \left\{ exp\left(\frac{\overleftarrow{\alpha} F}{R T} \eta_{HER}(T,P)\right) - exp\left(\frac{\overrightarrow{\alpha} F}{R T} \eta_{HER}(T,P)\right) \right\} \tag{3}$$

$j_{OER}^0(T, P)$ is the apparent current density of the OER at the anode. This is the product of the real exchange current density $j_{OER}^{0,*}(T, P)$ (the reference value for IrO$_2$ in acidic media is 5x10^{-6} A.cm^{-2}) and the roughness factor r_{OER}^f of the anode. $j_{HER}^0(T, P)$ is the apparent current density of the HER at the cathode. This is the product of the real exchange current density $j_{HER}^{0,*}(T, P)$ (the reference value for Pt° in acidic media is 1x10^{-3} A.cm^{-2}) and the roughness factor r_{HER}^f of the cathode. Experimental i-V curves can be fitted using the model Eqs 1–3 to obtain the roughness factors of half-cell reactions, and the cell resistances as well. The roughness factor and exchange current density of MEA anode was assumed to be a constant, because the same anodes were used in all the experiments.

TABLE S1 Parameters used in Eq. (1) for fitting of the experimental i–V curves shown in Figure 1-B, which were measured at T = 80°C ($\bar{\alpha} = \vec{\alpha} = 0.5$)

Electro(pre)catalyst	$R_{cell} = \sum_k R_k$ $(m\Omega. cm^2)$	$j_{OER}^{0,*}$ A.cm^{-2}	r_{OER}^f adim	$j_{HER}^{0,*}$ A.cm^{-2}	r_{HER}^f adim
1	635	5x10^{-6}	50	1x10^{-3}	0.05
2	635	5x10^{-6}	50	1x10^{-3}	0.2
3	405	5x10^{-6}	50	1x10^{-3}	3.0

TABLE S2 Parameters used in Eq. (1) for fitting of the experimental i–V curves shown in Figure 2-A ($\bar{\alpha} = \vec{\alpha} = 0.5$)

Cathode material	$R_{cell} = \sum_k R_k$ $(m\Omega. cm^2)$	$j_{OER}^{0,*}$ A.cm^{-2}	r_{OER}^f adim	$j_{HER}^{0,*}$ A.cm^{-2}	r_{HER}^f adim
CP	1155	5x10^{-6}	50	1x10^{-3}	0.05
1/CP	395	5x10^{-6}	50	1x10^{-3}	2.2
2/CP	305	5x10^{-6}	50	1x10^{-3}	28.0
3/CP	305	5x10^{-6}	50	1x10^{-3}	5.5
Pt-C/CP	187	5x10^{-6}	1200	1x10^{-3}	1200

References

S1. A.V. Dolganov, I.G. Belaya and Y.Z. Voloshin, *Electrochim. Acta.*, 2014, **125**, 302.

S2. Y.Z. Voloshin, V.V. Novikov, Y.V. Nelyubina, A.S. Belov, D.M. Roitershtein, A. Savitsky, A. Mokhir, J. Sutter, M.E. Miehlich and K. Meyer, *Chem. Commun.*, 2018, **54**, 3436.

S3. D. Kochubey, V. Kaichev, A. Saraev, S. Tomyn, A. Belov and Y. Voloshin, *J. Phys. Chem. C*, 2013, **117**, 2753.

S4. Y.Z. Voloshin, N.V. Chornenka, A.S. Belov, S.A. Grigoriev, A.S. Pushkarev, P. Millet, V.N. Kalinichenko, I.G. Belaya, M.G. Bugaenko and A.G. Dedov, *Macroheterocycles*, 2018, **11**, 449.

S5. Y. Z. Voloshin, N. V. Chornenka, A. S. Belov, S. A. Grigoriev, A. S. Pushkarev, P. Millet, V. N. Kalinichenko, D. A. Oranskiy and A. G. Dedov, *J. Electrochem. Soc.*, 2019, **166**, H598.

S6. S.A. Grigoriev, P. Millet, K.A. Dzhus, H. Middleton, T.O. Saetre and V.N. Fateev, *Int. J. Hydrogen Energy*, 2010, **35**, 5070.

S7. A.S. Pushkarev, M.A. Solovyev, S.A. Grigoriev, I.V. Pushkareva, Y.Z. Voloshin, N.V. Chornenka, A.S. Belov, P. Millet, V.N. Kalinichenko, A.G. Dedov, *Int. J. Hydrogen Energy*, 2020, **45**, 26206.

S8. S.A. Grigoriev, A.S. Pushkarev, I.V. Pushkareva, P. Millet, A.S. Belov, V.V. Novikov, I.G. Belaya and Y.Z. Voloshin, *Int. J. Hydrogen Energy*, 2017, **42**, 27845.

S9. S.V. Akel'kina, A.S. Pushkarev, S.A. Grigoriev, I.V. Pushkareva and V.N. Fateev, *Russ. J. Electrochem.*, 2018, **54**, 251.

S10. O.A. Varzatskii, D.A. Oranskiy, S.V. Vakarov, N.V. Chornenka, A.S. Belov, A.V. Vologzhanina, A.A. Pavlov, S.A. Grigoriev, A.S. Pushkarev, P. Millet, V.N. Kalinichenko, Y.Z. Voloshin and A.G. Dedov, *Int. J. Hydrogen Energy*, 2017, **42**, 27894.

S11. R. Valiollahi, M. Vagin, V. Gueskine, A. Singh, S.A. Grigoriev, A.S. Pushkarev, I.V. Pushkareva, M. Fahlman, X. Liu, Z. Khan, M. Berggren, I. Zozoulenko and X. Crispin, *Sustain. Energy Fuels*, 2019, **3**, 3387.

S12. S.A. Grigoriev, P. Millet and V.N. Fateev, *J. Power Sources*, 2008, **177**, 281.

S13. P. Millet, *ECS Transaction*, 2016, **75**, 28.

S14. J. O'M. Bockris and A.K.N. Reddy, *Modern Electrochemistry*, Plenum Press, New York, 1970.