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

**Artem S. Pushkarev,**[a] **Irina V. Pushkareva,**[a] **Maksim A. Solovyev,**[a,b] **Sergey A. Grigoriev,***[a,b,c,d]
**Yan Z. Voloshin,**[c,e,f] **Nina V. Chornenka,**[g] **Alexander S. Belov,**[c] **Pierre Millet,**[h] **Manuel Antuch,**[h]
**Valery N. Kalinichenko**[i] **and Alexey G. Dedov**[e,f]

[a] *National Research Center 'Kurchatov Institute', 123182 Moscow, Russian Federation.*
*E-mail: sergey.grigoriev@outlook.com*
[b] *National Research University 'Moscow Power Engineering Institute', 111250 Moscow, Russian Federation*
[c] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation*
[d] *HySA Infrastructure Center of Competence, Faculty of Engineering, North-West University, 2531 Potchefstroom, South Africa*
[e] *I. M. Gubkin Russian State University of Oil and Gas, 119991 Moscow, Russian Federation*
[f] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*
[g] *V. I. Vernadsky Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, 03142 Kyiv, Ukraine*
[h] *Institut de Chimie Moléculaire et des Matériaux d'Orsay, Université Paris-Saclay, 91405 Orsay, France*
[i] *N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

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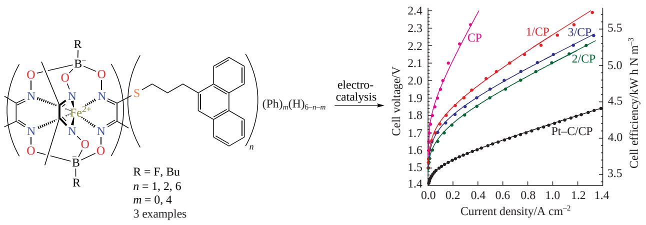
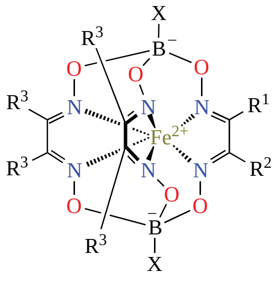
**Hydrogen-evolving cathodes were prepared using a series of iron(II) clathrochelates bearing various number of terminal phenanthrenyl groups *via* physisorption on carbon paper and employed in the polymer electrolyte membrane water electrolysis cells instead of typically used platinum. *In situ* electrochemical activation of the cathodes was carried out, after that the cells performance and durability were evaluated. These clathrochelate complexes represent a promising alternative to platinum as hydrogen-evolving cathode electrocatalysts.**



*Keywords*: macrocyclic compounds, clathrochelates, hydrogen evolution reaction, polymer electrolyte membrane, water electrolysis, electrocatalyst.

Molecular catalysts consisting of abundant elements are regarded as promising active components for the water electrolysis technology based on both the proton[1] and anion[2] exchange membranes. These catalysts can be used instead of the platinum group metal ones for the corresponding electrode processes.[3,4] However, their immobilization and an assembly of the working electrodes with high catalytic efficiency remain an experimental challenge.[3,5] Over the past two decades, cage transition metal complexes (clathrochelates[6]) have been extensively tested as electrocatalysts for the hydrogen evolution reaction (HER) in organic and aqueous acidic media.[7–10] The HER mechanism is still under discussion. The use of the encapsulating ligands with electron-withdrawing ribbed substituents in the clatrochelate complexes allows one[11] to stabilize their reduced forms, namely the metal(I) cage compounds, which have been proposed[7] as catalytically active intermediates in the multistep HER mechanism resulting in the reduction of $H^+$ ions into $H_2$ in acidic aqueous solutions. For example, the Co$^I$-encapsulating clathrochelate transient species,[8,9] formed after electroreduction of the corresponding Co$^{II}$ complexes, afford cobalt hydrides Co$^I$–H as the most probable catalytic HER intermediates. However, the clathrochelates considered are not generally stable under harsh conditions and decompose during the cathodic polarization and hydrogen evolution, resulting in nanoparticles of cobalt or cobalt alloy. For instance, an electrochemical reduction of the macrobicyclic cobalt(II) dioximates in the HER process is accompanied by the *in situ* formation of catalytically active metal nanoparticles.[12–14] Considering iron as an abundant and cheap metal, its macrobicyclic polyazomethine complexes bearing various functional terminal groups are synthetically available, stable in harsh acidic media and represent the effective HER electrocatalysts.[8,10] Recently, cobalt and iron clathrochelates have been immobilized [10,15–17] by physisorption on the surface of cathodes based on carbon paper (CP). In this work, we explored a series of polyaromatic-terminated iron(II) clathrochelates **1–3** with one, two and six phenanthrene moieties, physisorbed on the surface of CP at the cathode of the polymer electrolyte membrane (PEM) water electrolysis (WE) cells.

The complexes **1–3** were synthesized as described.[15,16] Gas diffusion electrodes (GDEs) based on CP were modified by the



**1–3**

**1** X = F, $R^1$ = 3-(9-phenanthrenyl)propylsulfanyl, $R^2$ = H, $R^3$ = Ph
**2** X = F, $R^1 = R^2$ = 3-(9-phenanthrenyl)propylsulfanyl, $R^3$ = Ph
**3** X = Bu, $R^1 = R^2 = R^3$ = 3-(9-phenanthrenyl)propylsulfanyl

clathrochelates and tested as the cathodes (for details, see Online Supplementary Materials). The GDE performance was benchmarked using their counterparts with the carbon-supported platinum nanoparticles.[15] The assembled PEM WE cells were activated using the known technique[18] by applying a constant voltage of 1.8, 2.0 or 2.2 V at 80 °C for 1.0–1.5 h until a constant current density was reached. This procedure was carried out to rearrange of an Ir/$IrO_x$ surface of the anodes[19] and to form the definite structure of the clathrochelate-containing cathodes, as detailed below. An effect of such activation on the cell performance is demonstrated in Figure 1 using complex **1**.

As follows from the chronoamperometry curves [Figure 1(*a*)], the cell current gradually increases before reaching of a plateau value, which corresponds to complete activation. The current–voltage curves [Figure 1(*b*)] are substantially different, the better performance is attained for the cells activated at higher voltage. The beneficial effect of such activation is clearly observed in a current density range below 0.1 A $cm^{-2}$, where the ohmic losses are negligible. In a high current density range with domination of the ohmic resistance, the polarization curves represent linear regressions with their similar slopes. The experimental current–voltage curves were fitted using the model equations, the obtained best fitting parameters are presented in the Online Supplementary Materials. The fitting results suggest a decrease in the total cell resistance and an increase in the roughness factor for the cathodes at higher applied cell voltage.

Figure 1(*c*) demonstrates the Tafel plots after an ohmic potential drop (*iR*) correction[20,21] measured at current density up to 100 mA $cm^{-2}$ with both the anode and cathode contributions being taken into account.[22] The Tafel plot slopes, which have been measured per logarithmic decade, decrease from 170 to 124 mV $dec^{-1}$ with increase in an activation voltage from 1.8 to 2.2 V. This originates from a substantial decrease in the HER overpotential during the cathode activation phase, probably because of a gradual electrosorption of these complexes onto carbon fibers during the polarization stage and/or their partial destruction resulting in the catalytically active metallocenters at an atomic level, *i.e.*, so-called single-atom catalysts.[23]

Then, a catalytic activity of the clathrochelates **1–3** in the HER was studied. The resulting experimental current–voltage curves are collected in Figure 2(*a*). At a current density of 1.0 A $cm^{-2}$ representing the benchmark value for PEM electrolyzers,[24,25] the cell voltages are *ca.* 2.24, 2.10 and 2.15 V for the CP-based cathodes with immobilized complexes **1**, **2** and **3**, respectively. These values are close to those obtained[10,18] for the same PEM electrolysis cell using the hexaphenanthrenyl-terminated cobalt, ruthenium and iron(II) clathrochelates, while they are still substantially higher than the value of 1.75 V that was obtained using metallic platinum. Nevertheless, the results obtained are encouraging. Electrocatalytic efficiency of the complexes **1–3** is affected by the number of their terminal phenanthrenyl group(s) per a clathrochelate molecule; a reason is probably their different physisorption on a particular CP material, the lowest cell voltage being revealed by the diphenanthrenyl-terminated complex **2**.

The curves shown in Figure 2(*a*) were fitted using the model equations; for the obtained best fitting parameters see the Online Supplementary Materials. When bare CP was used as a cathode, the cell performance was poor due to a strong contact resistance between CP and the membrane, as well as a low bare carbon HER activity, resulting in a high total cell resistance. In the presence of these clathrochelates, the cell resistance was much lower because of their better contact with membrane and the substantially higher values of the corresponding roughness factors. Using complex **2**, the best performance was obtained with an apparent HER current density of $2.8 \times 10^{-2}$ A $cm^{-2}$. However, this value is 43 times less than that of 1.2 A $cm^{-2}$ for metallic platinum at the same voltage.

To compare the specific activities of **1–3**, the above experimental current–voltage curves were *iR* corrected and the current densities were normalized per one μmol of the corresponding complex at the CP-based cathode [Figure 2(*b*)]. The best performance was again observed for the clathrochelate **2** bearing two terminal phenanthrenyl groups. The cell voltages required for obtaining of the reference value of 1.0 A $\mu mol^{-1}$ are 1.76, 1.67 and 1.73 V for **1**, **2** and **3**, respectively. The Tafel slope for the reference platinum-containing PEM cell is *ca.* 73 mV $dec^{-1}$ [Figure 2(*c*)]. Assuming the Volmer–Tafel mechanism of the electrocatalytic HER,[26] the contribution of Pt–C/CP to the above value is *ca.* 30 mV $dec^{-1}$. So, the contribution of the corresponding oxygen evolution reaction (OER), calculated as a difference between a whole value and that of the HER, is *ca.* 43 mV $dec^{-1}$,[18] thus being in good agreement

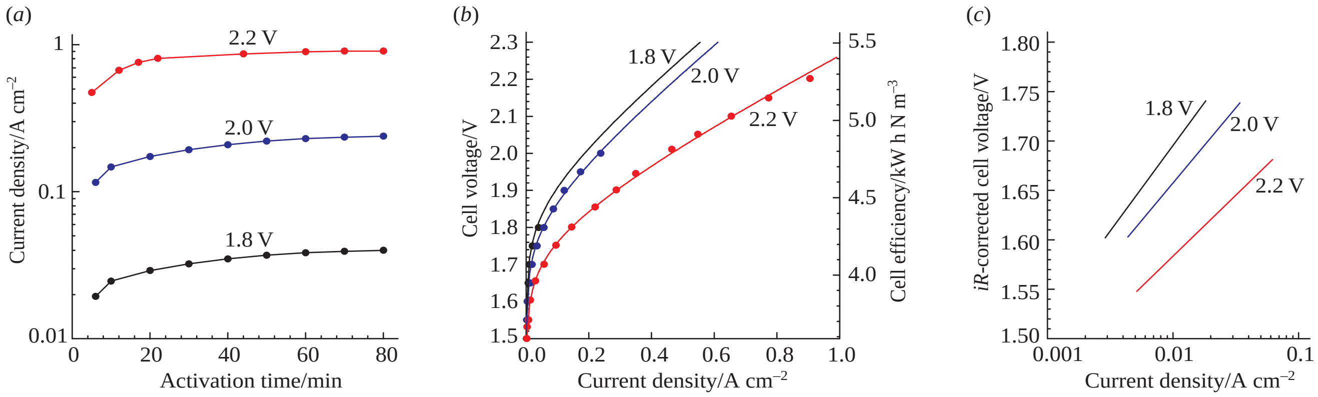


**Figure 1** Effect of an activation procedure at the different voltages on a performance of the cell equipped with clathrochelate **1**: (*a*) chronoamperometry curves measured during the cell activation; (*b*) current–voltage curves obtained after an activation; (*c*) Tafel plots at the low current densities after *iR* correction (see the text for details).

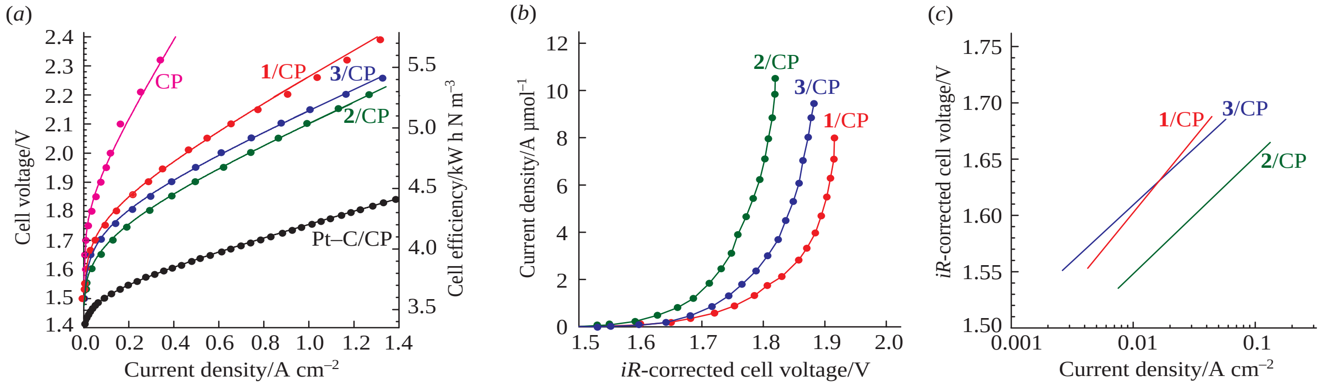


**Figure 2** Catalytic activity of the clathrochelates **1**–**3** immobilized on CP in PEM WE cells: (*a*) current–voltage curves at 80 °C compared with bare CP and metallic platinum on CP; (*b*) *iR*-corrected current–voltage curves per µmol of a given clathrochelate and (c) the corresponding Tafel plots.

with the known data.[27,28] The Tafel slopes for the cells with immobilized complexes **1**, **2** and **3** are 124, 106 and 90 mV dec$^{-1}$, respectively. Using the same subtraction of the above OER contribution, the HER Tafel slopes for the corresponding clathrochelate-containing cathodes are 81, 63 and 47 mV dec$^{-1}$, which are slightly lower than those observed[18] for iron, cobalt and ruthenium(II) clathrochelates with six phenanthrenyl groups under the same experimental conditions and in good agreement with those obtained[29,30] for iron and cobalt nanoparticles in 0.1 M aqueous $H_2SO_4$. Recent XANES/EXAFS data[31] suggested a formation of the cobalt(I)- and iron(I)-encapsulating reduced forms of the catalysts, in contrast to the corresponding atomic level metal(0)-based centers[32] in the catalytic syngas production, thus clarifying the clathrochelate-electrocatalyzed mechanism of the HER. On the other hand, the experimental Tafel slopes can be affected by various other factors, such as a surface coverage by the catalytically active intermediates, transfer coefficient, temperature, the type of electrolyte, *etc*.[33] So, it is still hard to make the reasonable and reliable suggestions on the HER mechanism in these hydrogen-producing systems.[23,34,35] Due to the initial voltage-dependent performance found for the clathrochelate-containing PEM WE cells, their durability was examined according to the known approach[36] at an applied constant voltage of 2.2 V for 24 h. The corresponding membrane electrode assemblies (MEAs) demonstrated a reasonable stability with the current density drops of 0.05–0.07 A cm$^{-2}$, comparable with those obtained for other promising non-platinum HER electrocatalysts, such as nickel and molybdenum sulfides and phosphides tested in PEM water electrolyzers.[37–39] However, the current density drop values obtained are still higher than that for the reference Pt–C/CP-based MEA, namely less than 0.015 A cm$^{-2}$ at 1.75 V and an initial current density of 1.0 A cm$^{-2}$.

In summary, the designed phenanthrenyl-terminated iron(II) clathrochelates physisorbed on CP cathodes were tested as the HER electrocatalysts in PEM cells of a water electrolyzer. Their electrochemical performance was substantially improved by *in situ* electrochemical activation at a constant applied cell voltage and was found to be slightly affected by the number of their terminal phenanthrenyl group(s); the best values of performance and stability of these cells were observed for the diphenanthrenyl clathrochelate. These designed complexes are the derivatives of iron as the most abundant metal and are quite inexpensive, though they cannot still fully compete with metallic platinum used here as the reference catalyst. Nevertheless, the experimentally observed performance of these clathrochelates is encouraging and comparable with that of the most promising non-platinum HER electrocatalysts reported to date.

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### *Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.01.005.

## References

1 K. Ayers, *Curr. Opin. Electrochem.*, 2019, **18**, 9.
2 I. Vincent and D. Bessarabov, *Renewable Sustainable Energy Rev.*, 2018, **81**, 1690.
3 B. Zhang, L. Fan, R. B. Ambre, T. Liu, Q. Meng, B. J. J. Timmer and L. Sun, *Joule*, 2020, **4**, 1408.
4 X. Sun, K. Xu, C. Fleischer, X. Liu, M. Grandcolas, R. Strandbakke, T. S. Bjørheim, T. Norby and A. Chatzitakis, *Catalysts*, 2018, **8**, 657.
5 Q. Liu, X. Liu, L. Zheng and J. Shui, *Angew. Chem., Int. Ed.*, 2018, **57**, 1204.
6 Y. Voloshin, I. Belaya and R. Krämer, *Cage Metal Complexes. Clathrochelates Revisited*, Springer, Heidelberg, 2017.
7 O. Pantani, S. Naskar, R. Guillot, P. Millet, E. Anxolabéhère-Mallart and A. Aukauloo, *Angew. Chem., Int. Ed.*, 2008, **47**, 9948.
8 A. V. Dolganov, A. S. Belov, V. V. Novikov, A. V. Vologzhanina, A. Mokhir, Y. N. Bubnov and Y. Z. Voloshin, *Dalton Trans.*, 2013, **42**, 4373.
9 V. S. Thoi, Y. Sun, J. R. Long and C. J. Chang, *Chem. Soc. Rev.*, 2013, **42**, 2388.
10 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.
11 G. E. Zelinskii, A. A. Pavlov, A. S. Belov, I. G. Belaya, A. V. Vologzhanina, Y. V. Nelyubina, N. N. Efimov, Y. V. Zubavichus, Y. N. Bubnov, V. V. Novikov and Y. Z. Voloshin, *ACS Omega*, 2017, **2**, 6852.
12 E. Anxolabéhère-Mallart, C. Costentin, M. Fournier, S. Nowak, M. Robert and J.-M. Savéant, *J. Am. Chem. Soc.*, 2012, **134**, 6104.
13 E. Anxolabéhère-Mallart, C. Costentin, M. Fournier and M. Robert, *J. Phys. Chem. C*, 2014, **118**, 13377.
14 B. Lassalle-Kaiser, A. Zitolo, E. Fonda, M. Robert and E. Anxolabéhère-Mallart, *ACS Energy Lett.*, 2017, **2**, 2545.
15 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.
16 Y. Z. Voloshin, N. V. Chornenka, O. A. Varzatskii, A. S. Belov, S. A. Grigoriev, A. S. Pushkarev, P. Millet, V. N. Kalinichenko, I. G. Belaya, M. G. Bugaenko and A. G. Dedov, *Electrochim. Acta*, 2018, **269**, 590.

17 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.
18 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 and A. G. Dedov, *Int. J. Hydrogen Energy*, 2020, **45**, 26206.
19 S. M. Alia and G. C. Anderson, *J. Electrochem. Soc.*, 2019, **166**, F282.
20 S. Siracusano, V. Baglio, A. Di Blasi, N. Briguglio, A. Stassi, R. Ornelas, E. Trifoni, V. Antonucci and A. S. Aricò, *Int. J. Hydrogen Energy*, 2010, **35**, 5558.
21 A. Weiß, A. Siebel, M. Bernt, T.-H. Shen, V. Tileli and H. A. Gasteiger, *J. Electrochem. Soc.*, 2019, **166**, F487.
22 H. Ito, T. Maeda, A. Nakano, A. Kato and T. Yoshida, *Electrochim. Acta*, 2013, **100**, 242.
23 Y. Z. Voloshin, V. M. Buznik and A. G. Dedov, *Pure Appl. Chem*., 2020, **92**, 1159.
24 M. Carmo, D. L. Fritz, J. Mergel and D. Stolten, *Int. J. Hydrogen Energy*, 2013, **38**, 4901.
25 G. Bender, M. Carmo, T. Smolinka, A. Gago, N. Danilovic, M. Mueller, F. Ganci, A. Fallisch, P. Lettenmeier, K. A. Friedrich, K. Ayers, B. Pivovar, J. Mergel and D. Stolten, *Int. J. Hydrogen Energy*, 2019, **44**, 9174.
26 J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry. An Introduction to an Interdisciplinary Area*, Plenum Press, New York, 1970.
27 P. Lettenmeier, L. Wang, U. Golla-Schindler, P. Gazdzicki, N. A. Cañas, M. Handl, R. Hiesgen, S. S. Hosseiny, A. S. Gago and K. A. Friedrich, *Angew. Chem., Int. Ed.*, 2016, **55**, 742.
28 H.-S. Oh, H. N. Nong, T. Reier, M. Gliech and P. Strasser, *Chem. Sci*., 2015, **6**, 3321.
29 J. Deng, P. Ren, D. Deng, L. Yu, F. Yang and X. Bao, *Energy Environ. Sci*., 2014, **7**, 1919.
30 M. Tavakkoli, T. Kallio, O. Reynaud, A. G. Nasibulin, C. Johans, J. Sainio, H. Jiang, E. I. Kauppinen and K. Laasonen, *Angew. Chem., Int. Ed*., 2015, **54**, 4535.
31 Ya. V. Zubavichus, S. A. Grigor'ev, A. S. Pushkarev, M. M. Borisov, M. G. Bugaenko, Ya. Z. Voloshin and A. G. Dedov, *Nanotechnologies in Russia*, 2020, **15**, 341 (*Ross. Nanotekhnol.*, 2020, **15**, 352).
32 A. G. Dedov, Ya. Z. Voloshin, A. S. Belov, A. S. Loktev, A. S. Bespalov and V. M. Buznik, *Mendeleev Commun*., 2019, **29**, 669.
33 T. Shinagawa, A. T. Garcia-Esparza and K. Takanabe, *Sci. Rep*., 2015, **5**, 13801.
34 J. Al Cheikh, A. Villagra, A. Ranjbari, A. Pradon, M. Antuch, D. Dragoe, P. Millet and L. Assaud, *Appl. Catal., B*, 2019, **250**, 292.
35 S. Anantharaj, S. R. Ede, K. Karthick, S. S. Sankar, K. Sangeetha, P. E. Karthik and S. Kundu, *Energy Environ. Sci.*, 2018, **11**, 744.
36 P. Aßmann, A. S. Gago, P. Gazdzicki, K. A. Friedrich and M. Wark, *Curr. Opin. Electrochem*., 2020, **21**, 225.
37 J. Kim, J. Kim, H. Kim and S. H. Ahn, *ACS Appl. Mater. Interfaces*, 2019, **11**, 30774.
38 J. W. D. Ng, T. R. Hellstern, J. Kibsgaard, A. C. Hinckley, J. D. Benck and T. F. Jaramillo, *ChemSusChem*, 2015, **8**, 3512.
39 J. H. Kim, H. Kim, J. Kim, H. J. Lee, J. H. Jang and S. H. Ahn, *J. Power Sources*, 2018, **392**, 69.

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