ChemComm

Copper(II) tetrakis(pentafluorophenyl)porphyrin: Highly Active Copper-based Molecular Catalyst for Electrochemical CO2 Reduction

Journal:	*ChemComm*
Manuscript ID	CC-COM-10-2021-005880.R1
Article Type:	Communication

SCHOLARONE™
Manuscripts

COMMUNICATION

Copper(II) tetrakis(pentafluorophenyl)porphyrin: Highly Active Copper-based Molecular Catalyst for Electrochemical CO_2 Reduction

Kento Kosugi, [a‡] Hina Kashima, [a‡] Mio Kondo [*abc] and Shigeyuki Masaoka [*ab]

We report a highly active copper-based catalyst for electrochemical CO_2 reduction. Electrochemical analysis revealed that the maximum turnover frequency for CO_2 to CO conversion reached to 1,460,000 s^{-1} at an overpotential (η) of 0.85 V. Surprisingly, this value is more than 1,000,000 times higher than those of the other reported copper-based molecular catalysts.

The catalytic reduction of CO_2 in fuels or commodity chemicals is one of the most important technologies for constructing a renewable energy system.[1] For this purpose, extensive efforts have been made to develop catalytic systems for the reduction of CO_2.[2-4,5a] Among them, homogeneous molecular catalysts have an advantage in catalyst design at the molecular level based on the detailed mechanistic study. To date, many examples of metal-complex-based homogeneous catalysts have been reported.[2-4] In particular, earth-abundant first-row transition metals have attracted attention as a constituent element of the catalyst.[3a-3n,4]

In this context, copper has attracted significant attention because it is earth-abundant, inexpensive and non-toxic. In addition, it facilitates CO_2 capture and activation.[5a-5c] Actually, it has been reported that copper electrodes can efficiently catalyze electrochemical CO_2 reduction in aqueous media, and afford highly reduced species such as methane, ethane, and ethanol.[5a] Followed by this pioneering work, heterogeneous copper-based catalysts have intensively been studied in recent years.[5d] However, reports on copper-based homogeneous molecular catalyst for CO_2 reduction have been limited.[4] Moreover, the catalytic activities of copper complexes for CO_2

reduction are much lower (turnover frequency (TOF) ≤ 1.1 s^{-1})[4e] than those of the reported molecular catalysts based on manganese (5,011 s^{-1}),[3m] iron (7,300,000 s^{-1}),[3i] cobalt (33,000 s^{-1}),[3k] and nickel (190 s^{-1}).[3n] These limitations associated with the copper-based CO_2 reduction catalysts have prompted us to explore a new copper-based molecular catalyst with high performance.

Here, we report a copper-based molecular catalyst that exhibits highly active electrochemical CO_2 reduction. Electrochemical analysis revealed that the TOF value for CO_2 to CO conversion was the highest among the copper-based molecular catalysts. The catalytic Tafel plot[6] also indicated that the TOF value was high even at a very low overpotential, which is superior to that of most molecular catalysts reported so far.

We assumed that the following three factors are crucial for constructing an efficient catalytic system for electrochemical CO_2 reduction. First, the copper porphyrin complex is used as a scaffold; metal porphyrin complexes are considered as efficient scaffolds for catalysis owing to their flexible redox properties and robustness during the catalysis.[2b,3a-3i] Second, a strong electron-withdrawing substituent is introduced at the meso positions of the porphyrin framework; generally, strong electron-withdrawing groups are preferred in the electrochemical reduction reaction to lower the overpotential.[7] Finally, acetonitrile (MeCN) was used as the reaction medium; we previously reported that the catalytic activity of the iron(III) porphyrin complex is improved dramatically in MeCN than those in other solvents,[3i] and thus, we used MeCN herein.

As a candidate that satisfies all the aforementioned factors, we employed copper(II) tetrakis(pentafluorophenyl)porphyrin (**CuTPFP**) shown in Scheme 1. **CuTPFP** contains a copper porphyrin framework with pentafluorophenyl groups at the meso positions. Pentafluorophenyl groups act as strong electron-withdrawing substituents. In addition, **CuTPFP** is well soluble in MeCN because of these groups. The synthesis of **CuTPFP** was performed by modifying a previously reported

[a.] *Division of Applied Chemistry, Graduate School of Engineering Osaka University 2-1 Yamadaoka, Suita Osaka 565-0871, Japan. E-mail: mio@chem.eng.osaka-u.ac.jp, masaoka@chem.eng.osaka-u.ac.jp*

[b.] *Innovative Catalysis Science Division, Institute for Open and Transdiciplinary Research Initiatives (ICS-OTRI), Osaka University, Suita, Osaka 565-0871, Japan*

[c.] *PREST, Japan Science and Technology Agency (JST), 4-1-4 Honcho, Kawaguchi, Saitama 332-0012, Japan*
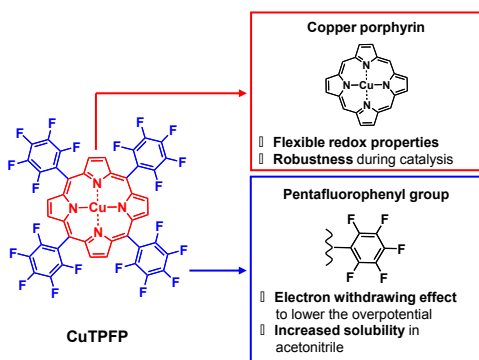
Scheme 1 Chemical structure and characteristics of **CuTPFP**.

method.[8] **CuTPFP** was characterized by elemental and single-crystal X-ray structural analysis (see experimental section, Fig. S1, and Table S1 in the ESI[†]).

Initially, the cyclic voltammetry of **CuTPFP** was measured in a 0.1 M tetra-n-butylammonium perchlorate (TBAP)/MeCN solution. Under Ar atmosphere, **CuTPFP** exhibited two redox waves at −1.32 V [vs. ferrocene/ferrocenium (Fc/Fc$^+$)] and −1.77 V (Fig. 1a, and Table S2). Due to the electron-withdrawing effect of the pentafluorophenyl group, the redox potentials of **CuTPFP** shifted to more positive potential than those of copper(II) tetraphenyl porphyrin, **CuTPP** (−1.64 V and −2.16 V, Fig. S2 and Table S2). Quantum chemical calculation also revealed that the LUMOs of **CuTPFP** are lower than those of **CuTPP**, indicating that **CuTPFP** can more easily be reduced than **CuTPP** (see also the ESI (P.S11) for details).The peak currents corresponding to these redox potentials of **CuTPFP** have a linear relationship with the square root of the scan rate and follow the Randles–Sevcik equation, indicating that **CuTPFP** can facilitate rapid electron transfer reactions (Fig. S3). Under CO_2 atmosphere in the presence of 1.0 M trifluoroethanol (TFE) as a proton source, **CuTPFP** exhibited a large irreversible current at −1.67 V, suggesting the electrocatalytic activity of the complex for CO_2 reduction (Fig. 1b, blue line).

To quantify the catalytic product, a controlled potential electrolysis (CPE) experiment of **CuTPFP** was performed in MeCN with 0.1 M TBAP, in the presence of 1.0 M TFE, under CO_2

at −2.39 V vs. Fc/Fc$^+$. In the CPE experiment, tetra-n-butyl ammonium acetate (TBAA) was added to the anodic chamber (Fig. S4) to promote the oxidation process on the Pt counter electrode. TBAA reacts at the anode to consume the holes and produce CO_2 and ethane via the Kolbe reaction.[3g] As a result, the total amount of charge passed over a period of 60 min was 72.4 C (Fig. 1c). The products of the reaction were also quantified by gas chromatography and high-performance liquid chromatography, and the formation of CO, HCOOH, and H_2 was confirmed with a Faradaic efficiency (FE) of 76.6% (287.4 μmol), 19.6% (73.5 μmol) and 1.7% (6.4 μmol), respectively. We also note the almost linear evolution of the charge during electrolysis, indicating no noticeable sign of catalyst degradation. After the CPE experiment, we performed a dynamic light scattering measurement of the solution and confirmed that there was no particle formation in the solution, which is evidence of the homogeneous nature of **CuTPFP** (Fig. S6). Additionally, the UV-absorption spectra of **CuTPFP** measured before and after the CPE experiment is almost identical (Fig. S7), and the no formation of the catalytically active heterogenous species was detected by the blank CPE experiment using the electrode after the electrolysis (Fig. S8 and Table S4, see the ESI (P.S16) for details). These results clearly demonstrate that **CuTPFP** can function as a robusthomogeneous CO_2 reduction catalyst.

To evaluate the catalytic activity of **CuTPFP**, a catalytic Tafel plot for CO production was then constructed.[6] In this study, TOFs were determined directly from the results of CPE experiments at varying applied potentials (Fig. S5 and Table S3). It is useful to benchmark the performance of a catalyst as a function of the overpotential (η); therefore, we converted the applied potentials into overpotentials. Here, $\eta = E_{CO2/CO} - E$ and $E_{CO2/CO} = -1.54$ V vs. Fc/Fc$^+$.[3h,9] As shown in Fig. 2, TOF increased as the overpotential increased and reached a plateau at $\eta = 0.66$ V (for details, please refer to the details provided on P.S17–S18 and Table S5). The TOF value of the plateau, corresponding to the intrinsic catalytic activity of the catalyst (TOF$_{max}$), was 1,460,000 s^{-1}. Surprisingly, this value is more than 1,000,000 times greater than those of other reported copper-based catalysts (Fig. 3 and Table 1). It should be noted that the TOF values of **CuTPFP** is significantly larger than that of a copper
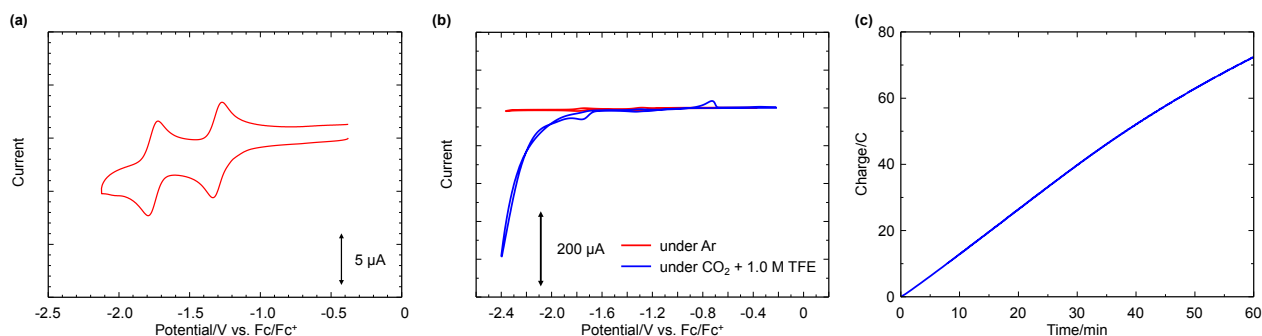

Fig. 1 (a) Cyclic voltammograms of **CuTPFP** (0.20 mM) in MeCN with TBAP (0.1 M) under Ar (scan rate: 100 mV s^{-1}). (b) Cyclic voltammograms of **CuTPFP** (0.20 mM) in MeCN with TBAP (0.1 M) in the presence of TFE (1.0 M) under CO_2 (scan rate: 100 mV s^{-1}). (c) Electrolysis data of **CuTPFP** (0.02 mM) in MeCN with TBAP (0.1 M) in the presence of TFE (1.0 M) under CO_2 at a potential of −2.39 V vs. Fc/Fc$^+$. Working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: Ag/Ag$^+$.
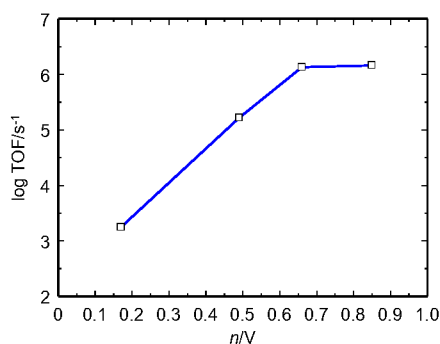
Fig. 2 Catalytic Tafel plot of **CuTPFP** in MeCN with TBAP (0.1 M) for CO_2 to CO conversion obtained from CPE experiments at varying overpotentials. Working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: Ag/Ag⁺.

porphyrin without pentafluorophenyl functional groups, **CuTPP** (18,200 s⁻¹, see also the ESI (P.S21-22) for details). We also calculated the turnover number (TON) of the catalytic reaction, and the value was reached to 5.26×10^9 (for the details of the determination of the TON, see the footnote of the Table S6).

We also compared the catalytic activity of **CuTPFP** with that of other metal-complex-based molecular catalysts. Table S6 shows that the TOF_{max} value of **CuTPFP** is comparable to that of current, high-performing metal-complex-based molecular catalysts for electrochemical CO_2 reduction. The catalytic Tafel plots of several metal-complex-based molecular catalysts also enabled the comparison of their TOFs, in terms of overpotential. As shown in Fig. 4, the TOF value of **CuTPFP** was 1,770 s⁻¹ at η = 0.17 V. This performance is superior to those of most metal-complex-based molecular catalysts, indicating that **CuTPFP** is an excellent catalyst, even at very low overpotentials. In other words, **CuTPFP** is a highly active electrocatalyst for CO_2 reduction from low to high overpotentials.

In summary, we have shown a copper-based homogeneous catalyst that exhibits highly active electrochemical CO_2 reduction. Herein, we selected **CuTPFP** as a copper-based molecular catalyst that satisfied the following three elements: (i) copper porphyrin as a scaffold, (ii) introduction of strong electron-withdrawing substituents, and (iii) soluble in MeCN as a reaction medium. CPE experiments indicated that **CuTPFP** functioned as a robust homogeneous CO_2 reduction catalyst. Furthermore, it exhibited a TOF value for CO production of 1,460,000 s⁻¹, which is more than 1,000,000 times higher than those of other reported copper-based catalysts. The catalytic Tafel plot for CO production revealed that the activity of **CuTPFP** was comparable to that of current best-in-class molecular catalysts across a wide range of overpotentials. The TOF value of **CuTPFP** at a low overpotential (1,770 s⁻¹ at η = 0.17 V) was superior than those of most catalysts, demonstrating the advantages of **CuTPFP**. We believe that the present study will open a new avenue for the development of efficient copper-based homogeneous catalysts for CO_2 reduction.

Table 1 TOFs of the copper-based molecular catalyst for CO_2 reduction.

Catalyst[a]	Media	Reductant	TOF / s⁻¹[b]	Reference
CuTPFP	0.1 M TBAP/MeCN, 1.0 M TFE	Electrochemical	$1.46 \times 10^{6[c]}$ (−2.39 V vs. Fc/Fc⁺)	This work
Cu1	THF[d]	pinB[e]	$1.39 \times 10^{-2[f]}$	4a
Cu2	THF	pinB	$2.78 \times 10^{-2[f]}$	4a
Cu3	0.1 M TBAP/MeCN	Electrochemical	$5.56 \times 10^{-4[c],[f]}$ (−1.7 V vs. Ag/AgCl)	4b
Cu4	MeCN/H_2O (v/v = 97:3), 0.1 M BIH[g]/TEOA[h] (15% v/v)	Photochemical (λ > 420 nm)	1.15	4e
Cu5	MeCN/H_2O (v/v = 4:1), 0.3 M TEOA	Photochemical (λ = 450 nm)	$2.75 \times 10^{-1[f]}$	4f
Cu6	MeCN/H_2O (v/v = 4:1), 0.3 M TEOA	Photochemical (λ = 400 nm)	$8.40 \times 10^{-1[f]}$	4g

[a] The chemical structures of **Cu1**–**Cu6** are shown in Fig. 3. [b] The TOF value cannot be directly compared without recognizing that reaction conditions such as solvent, reductant, and applied potential differ. [c] Calculated from CPE data. [d] THF = tetrahydrofuran [e] pinB = 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane. [f] TOF was calculated by dividing the turnover number by the time during catalysis. [g] BIH = 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole. [h] TEOA = triethanolamine.
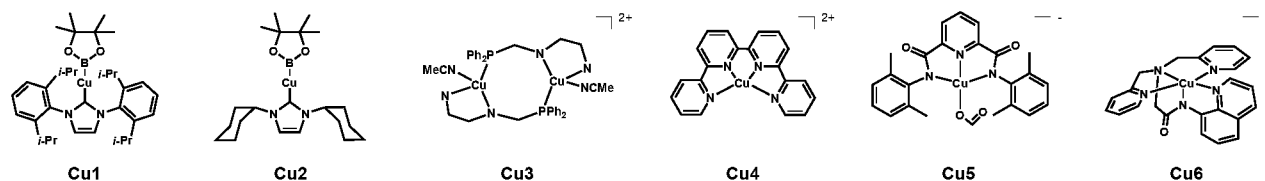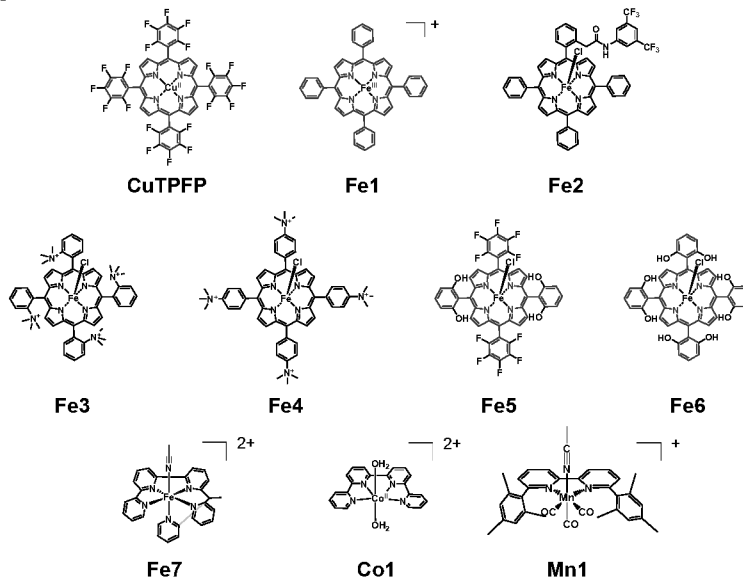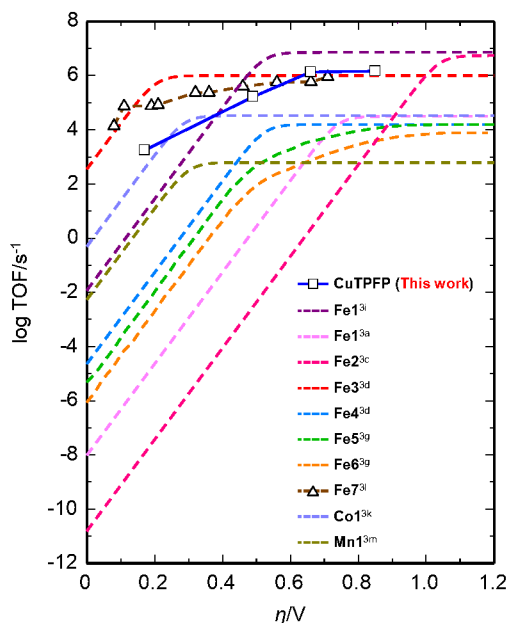

Cu1   **Cu2**   **Cu3**   **Cu4**   **Cu5**   **Cu6**

Fig. 3 Chemical structure of copper-based molecular catalysts for CO_2 reduction in Table 1.

Fig. 4 Benchmarking of the metal-complex-based molecular catalysts[3a,3c,3d,3g,3i,3k,3l,3m] of the CO_2 to CO electrochemical conversion by means of their catalytic Tafel plots.

Conflicts of interest

The authors declare no competing financial interest.

References

1 A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. A. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer, G. L. Waldrop, *Chem. Rev.*, 2013, **113**, 6621.

2 (a) R. Francke, B. Schille, M. Roemelt, *Chem. Rev.*, 2018, **118**, 4631. (b) E. Boutin, L. Merakeb, B. Ma, B. Boudy, M. Wang, J. Bonin, E. Anxolabéhère-Mallart, M. Robert, *Chem. Soc. Rev.*, 2020, **49**, 5772.

3 (a) C. Costentin, S. Drouet, G. Passard, M. Robert, J. M. Savéant, *J. Am. Chem. Soc.*, 2013, **135**, 9023. (b) C. Costentin, G. Passard, M. Robert, J. M. Savéant, *J. Am. Chem. Soc.*, **2014**, *136*, 11821. (c) E. M. Nichols, J. S. Derrick, S. K. Nistanaki, P. T. Smith, C. J. Chang, *Chem. Sci.*, 2018, **9**, 2952. (d) I. Azcarate, C. Costentin, M. Robert, J. M. Savéant, J. Am. *Chem. Soc.*, 2016, **138**, 16639. (e) E. A. Mohamed, Z. N. Zahran, Y. Naruta, *Chem. Commun.*, 2015, **51**, 16900. (f) Y. Okabe, S. K. Lee, M. Kondo, S. Masaoka, *J. Biol. Inorg. Chem.*, 2017, **22**, 713. (g) C. Costentin, G. Passard, M. Robert, J. M. Savéant, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 14990. (h) S. Sinha, J. J. Warren, *Inorg. Chem.*, **2018**, *57*, 12650. (i) K. Kosugi, M. Kondo, S. Masaoka, *Angew. Chem. Int. Ed.*, 2021, **60**, 22070. (j) W. Nie, D. E. Tarnopol, C. C. L. McCrory, *J. Am. Chem. Soc.*, 2021, **143**, 3764. (k) C. Cometto, L. Chen, P. K. Lo, Z. Guo, K. C. Lau, E. Anxolabéhère-Mallart, C. Fave, T. C. Lau, M. Robert, *ACS Catal.*, 2018, **8**, 3411. (l) J. S. Derrick, M. Loipersberger, R. Chatterjee, D. A. Iovan, P. T. Smith, K. Chakarawet, J. Yano, J. R. Long, M. Head-Gordon, C. J. Chang, *J. Am. Chem. Soc.*, 2020, **142**, 20489. (m) M. D. Sampson, C. P. Kubiak, *J. Am. Chem. Soc.*, 2016, **138**, 1386. (n) L. M. Cao, H. H. Huang, J. W. Wang,

D. C. Zhong, T. B. Lu, *Green Chem.*, 2018, **20**, 798. (o) S. K. Lee, M. Kondo, G. Nakamura, M. Okamura, S. Masaoka, *Chem. Commun.*, 2018, **54**, 6915. (p) K. Y. Wong, W. H. Chung, C. P. Lau, *J. Electroanal. Chem.*, 1998, **453**, 161.

4 (a) D. S. Laitar, P. Müller, J. P. Sadighi, *J. Am. Chem. Soc.*, 2005, **127**, 17196. (b) R. J. Haines, R. E. Wittrig, C. P. Kubiak, *Inorg. Chem.*, 1994, *33*, 4723. (c) R. Angamuthu, P. Byers, M. Lutz, A. L. Spek, E. Bouwman, *Science*, 2010, **327**, 313. (d) Y. Zhou, Y. Xiao, J. Zhao, *New J. Chem.*, 2020, **44**, 16062. (e) Z. Guo, F. Yu, Y. Yang, C. F. Leung, S. M. Ng, C. C. Ko, C. Cometto, T. C. Lau, M. Robert, *ChemSusChem,* 2017, **10**, 4009. (f) W. J. Liu, H. H. Huang, T. Ouyang, L. Jiang, D. C. Zhong, W. Zhang, T. B. Lu, *Chem. Eur. J.*, 2018, **24**, 4503. (g) X. Chai, H. H. Huang, H. Liu, Z. Ke, W. W. Yong, M. T. Zhang, Y. S. Cheng, X. W. Wei, L. Zhang, G. Yuan, *Chem. Commun.*, 2020, **56**, 3851.

5 (a) Y. Hori, H. Wakebe, T. Tsukamoto, O. Koga, *Electrochim. Acta*, 1994, **39**, 1833. (b) L. Liu, C. Zhao, Y. Li, *J. Phys. Chem. C*, 2012, **116**, 7904. (c) H. Yang, X. W. He, F. Wang, Y. Kang, J. Zhang, *J. Mater. Chem.*, 2012, **22**, 21849. (d) S. Nitopi, E. Bertheussen, S. B. Scott, X. Liu, A. K. Engstfeld, S. Horch, B. Seger, I. E. L. Stephens, K. Chan, C. Hahn, J. K. Norskøv, T. F. Jaramillo, I. Chorkendorff, *Chem. Rev.*, 2019, **119**, 7610.

6 (a) C. Costentin, S. Drouet, M. Robert, J. M. Savéant, *J. Am. Chem. Soc.*, 2012, **134**, 11235. (b) C. Costentin, J. M. Savéant, *ChemElectroChem*, 2014, **1**, 1226.

7 W. Zhang, W. Z. Lai, R. Cao, *Chem. Rev.*, 2017, **117**, 3717.

8 S. L. Rebelo, A. M. N. Silva, C. J. Medforth, C. Freire, *Molecules,* 2016, **21**, 481.

9 M. L. Pegis, J. A. S. Roberts, D. J. Wasylenko, E. A. Mader, A. M. Appel, J. M. Mayer, *Inorg. Chem.*, 2015, **54**, 11883.