Polymer Electrolyte Fuel Cells Hot Paper
Deutsche Ausgabe: DOI: 10.1002/ange.201607741
Internationale Ausgabe: DOI: 10.1002/anie.201607741

Oxygen-Tolerant Electrodes with Platinum-Loaded Covalent Triazine Frameworks for the Hydrogen Oxidation Reaction

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Abstract: *Reducing the use of platinum (Pt) on polymer electrolyte fuel cell anodes is critical for the widespread dissemination of these energy conversion systems. Although Pt usage can be minimized by the even dispersion of isolated Pt atoms, no atomically dispersed Pt catalysts that promote hydrogen oxidation at a rate required for practical fuel cells have been reported to date. Covalent triazine frameworks with atomically dispersed Pt atoms (0.29 wt %) are described and it is demonstrated that the material has a high electrocatalytic hydrogen oxidation activity without an overpotential. Importantly, when the loading amount was increased to 2.8 wt %, the electrocatalytic hydrogen oxidation activity of the resulting electrode was comparable to that of commercial carbon supported 20 wt % Pt catalysts, and the catalytic activity for oxygen reduction was markedly reduced. Thus, Pt-modified covalent triazine frameworks selectively catalyze hydrogen oxidation, even in the presence of dissolved oxygen, which is critical for limiting cathode degradation during the start–stop cycles of fuel cells.*

Polymer electrolyte fuel cells (PEFCs) that utilize hydrogen and oxygen as reactants have attracted considerable attention as environmentally friendly energy conversion systems, as they can be operated at relatively low temperature ($<100\,^{\circ}C$) and generate only water as the reaction product.[1] Currently, Pt or its alloys are typically used as the anode catalyst in PEFC systems.[2] However, because Pt is rare and expensive, reducing the loading amount of Pt on the anode is desirable for cost reduction.[3] Pt anode catalysts are also active for not only the hydrogen oxidation reaction (HOR), but also the oxygen reduction reaction (ORR).[2,4,5] This is problematic, because during the start-up of PEFCs air inevitably flows into the anode chamber and cathodic ORR proceeds on the Pt anode catalyst, leading to degradation of the cathode. The occurrence of ORR on Pt anode catalysts is a serious limitation of these systems, particularly for their use in vehicles, which have frequent start-up/shut-down cycles.[6,7] As a result of the limitations associated with Pt, improving the anode catalyst is essential for developing practical PEFC systems.

Atomically dispersed Pt-based catalyst (termed single-atom Pt catalyst) is a promising candidate for satisfying the requirements of PEFC anode catalysts. Because of the single-atom nature of the material, a high catalytic activity is likely achievable at lower Pt loading amounts, and additionally, unique reaction selectivity may be possible, as many types of reactions can only proceed on Pt ensemble sites.[8–10] Recently, we reported that covalent triazine frameworks (CTFs) can serve as a platform for single-atom electrocatalysts.[11] Although CTFs are non-conductive, we successfully developed a CTF-based electrocatalyst by hybridizing CTFs with conductive carbon particles.[11] As CTFs possess abundant nitrogen atoms with an electron lone pair, various metals can be loaded onto CTFs by coordination bonds with nitrogen. Using this approach, we demonstrated that atomic metal-loaded CTFs exhibit unique reaction activity and selectivity.[11,12]

Herein, we show that a Pt-modified CTF (Pt-CTF) has higher anodic HOR and lower cathodic ORR electrocatalytic activity compared to commercial Pt/C because of the abundance of atomically dispersed forms of Pt. These electrocatalytic properties suggest that Pt-CTF may be suitable as a PEFC anode catalyst for practical applications.

Pt-CTF was synthesized by polymerization of 2,6-dicyanopyridine in the presence of conductive carbon particles and subsequent impregnation of Pt in $K_2[PtCl_4]$ solution (Supporting Information, Experimental Section). Initially, we conducted physical characterizations of Pt-CTF, which was loaded with 0.29 and 2.8 wt % Pt. Commercial Pt cluster-loaded carbon (Pt/C) loaded with either 3.0 or 20 wt % Pt was used as a comparative reference. The surface compositions of Pt-CTF, 3.0 wt % Pt/C, and 20 wt % Pt/C, as estimated by X-ray photoelectron spectroscopy (XPS), BET surface area, and pore size, are summarized in Table 1. Pt L_3-edge extended X-ray absorption fine structure (EXAFS) analyses were also conducted (Supporting Information, Figure S1). Importantly, for the Fourier transformations of k^3-weighted EXAFS oscillations, the peak corresponding to the Pt−Pt bond at

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Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201607741.

Table 1: Physical characterization of the Pt-CTF and Pt/C catalysts.

Catalyst	Pt [wt%]	Pt [at%]	C [at%]	N [at%]	S_A [$m^2 g^{-1}$][a]	V_t [$cm^3 g^{-1}$][b]
0.29 wt% Pt-CTF	0.29	0.02	96	0.74	1060	2.72
2.8 wt% Pt-CTF	2.8	0.19	96	0.73	973	2.55
3.0 wt% Pt/C	3.0	0.21	93	–	530	1.22
20 wt% Pt/C	20	1.4	92	–	673	1.29

[a] BET surface area. [b] Total pore volume.

2.6 Å was not observed for either as-prepared 0.29 or 2.8 wt% Pt-CTF. Instead, two peaks at 1.6 and 2.0 Å were detected, which were respectively assigned to Pt–N and Pt–Cl bonds, indicating that Pt was dispersed in the form of single atoms in the as-prepared samples. The other examined physical properties of the Pt-CTF samples (Supporting Information, Figures S1–S5) were similar to those previously reported for Pt-CTF loaded with 12 wt% Pt.[11]

Pt-CTF in an Ar-purged $HClO_4$ solution was examined by cyclic voltammetry (CV; Supporting Information, Figure S6). The CVs for 3.0 and 20 wt% Pt/C catalysts were also determined as a reference. For the analysis, the amount of the entire catalyst loaded onto the electrode substrate was adjusted to approximately 0.050 mg cm^{-2} for all four samples. In the CVs, reversible peaks corresponding to the formation and desorption of under-potentially deposited hydrogen (upd-H) were observed for the Pt/C catalysts in the potential region of +0.02–+0.30 V,[13] but not for Pt-CTF. As the formation of upd-H proceeds at Pt ensemble sites (such as step, three-fold hollow, and defect sites),[14] these results further suggested that most of the Pt exists in an atomically dispersed form on the as-prepared Pt-CTFs. Additionally, no significant differences in the current density were observed between Pt-CTF and the two Pt/C catalysts in the potential region of +0.35–+0.40 V, where only charging and discharging of the electrical double layer occurs,[15] indicating that the electrochemically active surface area does not differ markedly among the four samples.

The electrocatalytic activity of 0.29 wt% Pt-CTF for HOR was evaluated by conducting linear sweep voltammetry (LSV) in an $HClO_4$ solution saturated with 1 atm H_2 (Figure 1 a). The current associated with the HOR started to flow at 0 V (that is, without an overpotential) and increased with a positive shift in the potential until reaching a peak at approximately 0.05 V. CTF without Pt did not generate a Faradaic current (Figure 1 a), indicating that the Pt loaded on CTF served as the HOR electrocatalyst. At a loading amount of 0.29 wt%, the possibility of Pt aggregate formation can be excluded.[8,9] Consistent with this speculation, no Pt aggregates were detected in the Fourier transformations of k^3-weighted EXAFS oscillations (Figure 2 a) or by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM; Figure 2 b), even after the LSV experiments. Taken together, these results clearly indicated that the HOR proceeds on single Pt atoms in Pt-CTF and requires almost no activation energy.

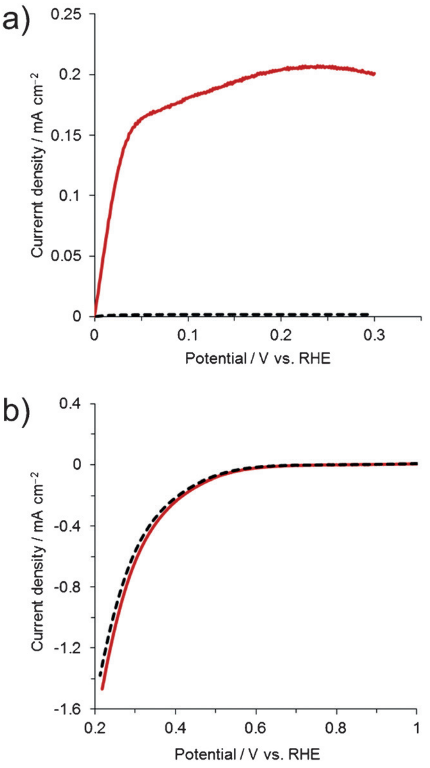

Figure 1. a) Polarization curves of 0.29 wt% Pt-CTF and CTF for the HOR (scan rate 5 mV s^{-1}, rotational rate 2500 rpm). b) Polarization curves of 0.29 wt% Pt-CTF and CTF for the ORR (scan rate 5 mV s^{-1}, rotational rate 1600 rpm). Key: 0.29 wt% Pt-CTF (——); CTF without Pt (-----). Conditions: the electrolyte (0.1 м $HClO_4$) was saturated with 1 atm O_2 at 25 °C.

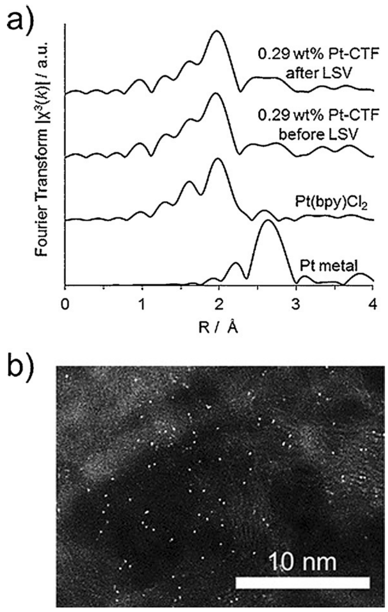

Figure 2. a) Fourier transformations of k^3-weighted Pt L_3-edge EXAFS oscillations and b) the corresponding HAADF-STEM image taken after the LSV measurement shown in Figure 1 a. Pt(bpy)Cl_2: dichloro(2,2′-bipyridine)platinum(II).

Subsequently, we investigated the electrocatalytic ORR activity of 0.29 wt% Pt-CTF. Figure 1 b shows the voltammograms of 0.29 wt% Pt-CTF and CTF in an $HClO_4$ solution saturated with 1 atm O_2. As the LSV trace of these two materials was similar, the ORR observed in the LSV analysis (Figure 1b) was confirmed to be catalyzed by the CTF substrate, demonstrating that the catalytic ORR activity of the Pt atoms on CTF was very low.

From these findings, it was revealed that the 0.29 wt% Pt-CTF had high and low catalytic activity for the HOR and ORR, respectively, a property that is advantageous for PEFC anode catalysts. However, as the loading amount was only 0.29 wt%, only a low current density was achieved for the HOR. Therefore, we prepared Pt-CTF with 2.8 wt% Pt and further examined the function of Pt-CTF as a PEFC-anode catalyst.

Similar to 0.29 wt% Pt-CTF, HOR current was first detected at 0 V (Figure 3a). The electrochemical performance of 2.8 wt% Pt-CTF was nearly identical to that of 20 wt% Pt/C (Figure 3a). However, 3.0 wt% Pt/C, generated a much lower HOR current than that of 2.8 wt% Pt-CTF (Figure 3a).

The HOR and hydrogen evolution reaction (HER) proceed on Pt via an identical reaction intermediate, and hence, these reactions are mutually reversible.[16,17] Therefore, Pt-CTF was expected to exhibit superior electrocatalytic activity even for the HER. To examine this assumption, LSVs for Pt-CTF, 3.0 wt% Pt/C, and 20 wt% Pt/C were measured in the potential range of 0 to −0.25 V, which corresponds to the range in which the HER proceeds (Figure S7). Similar to the HOR activity, the electrocatalytic HER activity of Pt-CTF was nearly identical to that of 20 wt% Pt/C, as expected.

In Fourier transformations of k^3-weighted EXAFS oscillations obtained after conducting the LSV experiments (Figure 3a), a small peak corresponding to a Pt−Pt bond was observed at 2.6 Å (Supporting Information, Figure S8), indicating the presence of aggregated Pt. However, reversible peaks corresponding to the formation and desorption of upd-H were not detectable (Supporting Information, Figure S9). These results indicate that, although some Pt formed aggregates, most Pt in 2.8 wt% Pt-CTF existed in an atomically dispersed form, even after the LSV analysis. It should be noted here that PEFCs are typically constructed with 20–50 wt% Pt/C as the anode catalyst.[4,18] Thus, the finding that 2.8 wt% Pt-CTF exhibits similar performance compared to 20 wt% Pt/C, owing to the efficient utilization of Pt atoms, is of high practical importance.

The electrocatalytic ORR activity of 2.8 wt% Pt-CTF was also investigated using a rotating ring-disc electrode (RRDE) technique (Figure 3c). Compared with 0.29 wt% Pt-CTF (Figure 1b), 2.8 wt% Pt-CTF exhibited higher ORR activity, a property that was likely due to the presence of Pt aggregates. However, the electrocatalytic ORR activity of 2.8 wt% Pt-CTF was markedly lower (Figure 3c) than that of commercial 20 wt% Pt/C (Figure 3c). Particularly in the potential region more positive than +0.6 V ($E > +0.6$ V), which is critical for the start-up/shut-down operation of PEFCs,[7] the ORR current for Pt-CTF was less than 23% of that generated by 20 wt% Pt/C. The lower ORR activity of the electrode prepared with 2.8 wt% Pt-CTF is attributed to the fact that only the 2 e^- pathway for generating hydrogen peroxide (H_2O_2) can proceed on a single Pt atom.[9,10,19]

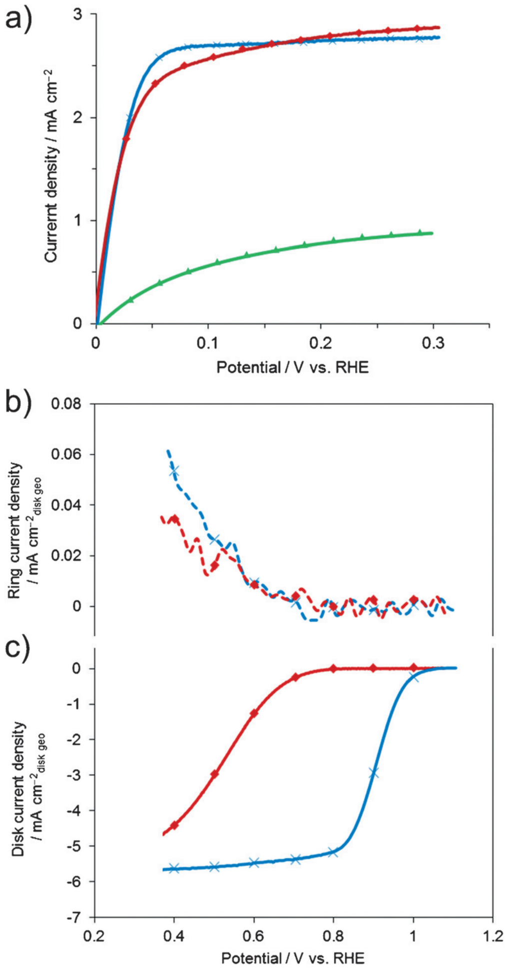

Figure 3. a) Polarization curves of 2.8 wt% Pt-CTF, 20 wt% Pt/C, and 3.0 wt% Pt/C for the HOR (scan rate 1 mVs^{-1}, rotational rate 2500 rpm). b) H_2O_2 oxidation currents recorded at 1.2 V vs. RHE on a ring electrode during the ORR on disc electrodes with the catalysts 20 wt% Pt/C and 2.8 wt% Pt-CTF. The currents were corrected by the collection efficiency of 0.424. c) Corresponding polarization curves for the ORR (conditions: sweep rate 10 mVs^{-1}, rotational rate 1600 rpm, 0.1 M $HClO_4$, 25 °C). Key: 2.8 wt% Pt-CTF (◆); 20 wt% Pt/C (×); 3.0 wt% Pt/C (▲).

Notably, the ring current, which corresponds to the generation of H_2O_2 as an ORR intermediate, did not significantly differ between the two catalysts at $E > +0.6$ V (Figure 3b). This property is critical for the long-term operation of PEFCs, as H_2O_2 can degrade PEFC components, such as membranes and catalyst binders.[20] Meanwhile, even in $E < +0.6$ V, the generation rate of H_2O_2 on Pt-CTF was comparable to that of Pt/C, indicating that most of the H_2O_2 generated on the single Pt atoms can be further reduced to water on the Pt clusters.

The HOR and ORR catalytic activities of the prepared electrodes were further investigated by chronoamperometry at +0.6 V (Figure 4). For the experiments, the input gas was switched from pure hydrogen to a mixed gas of hydrogen and oxygen (H_2:O_2 = 1:1) at 600 s. For 20 wt% Pt/C, the current changed from positive to negative when the input gas was altered. This change in the polarity likely occurred because the larger cathodic ORR current overlapped with the anodic HOR when oxygen was introduced into the system. In

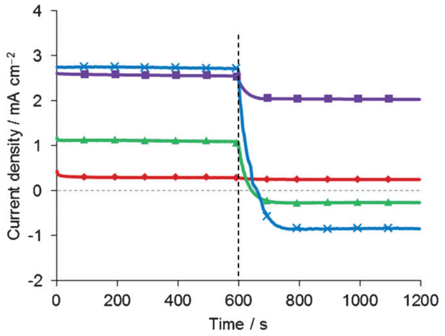

Figure 4. Chronoamperometric curves obtained in 0.1 M $HClO_4$ at +0.6 V vs. RHE for 20 wt% Pt/C (—×—), 2.8 wt% Pt-CTF (—■—), 3.0 wt% Pt/C (—▲—), and 0.29 wt% Pt-CTF (—◆—). Rotational rate: 2500 rpm. The input gas was altered at 600 s (L) from pure H_2 to a mixed gas consisting of H_2 and O_2 (H_2:O_2 = 1:1).

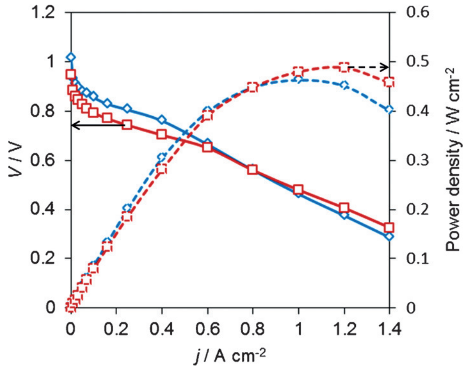

Figure 5. Fuel cell performance of MEAs. *j–V* curves (solid line) and *j*-power density curves (dashed line) for MEAs prepared using 2.8 wt% Pt-CTF or 20 wt% Pt/C as the anode catalyst. Both cathodes were loaded with 0.50 ± 0.01 $mg_{\text{-Pt}}\,cm^{-2}$. Key: 20 wt% Pt/C anode (loaded with 0.10 ± 0.01 $mg_{\text{-Pt}}\,cm^{-2}$; (—◇—)); 2.8 wt% Pt-CTF anode (loaded with 0.02 ± 0.001 $mg_{\text{-Pt}}\,cm^{-2}$; (—□—)). The data were collected at 80 °C and 100% relative humidity using H_2/O_2 as the reactants.

contrast, only a small decrease in current density was observed for 2.8 wt% Pt-CTF in the presence of the mixed gas. Importantly, such a clear decrease in the anodic current was not observed for 0.29 wt% Pt-CTF, which is predominantly comprised of only atomically dispersed Pt. Taken together, these results demonstrate that the electrode prepared with 2.8 wt% Pt-CTF selectively catalyzed the HOR, even in the presence of oxygen, and that this property was attributable to the high abundance of single Pt atoms on the catalytic substrate.

Finally, we evaluated the efficacy of 2.8 wt% Pt-CTF functioning as a PEFC anode catalyst. A membrane electrode assembly (MEA) was fabricated with 2.8 wt% Pt-CTF (0.020 ± 0.001 $mg_{\text{-Pt}}\,cm^{-2}$) and 47 wt% Pt/C (0.50 ± 0.01 $mg_{\text{-Pt}}\,cm^{-2}$) as the anode and cathode catalysts, respectively, and the performance of a PEFC ($PEFC_{Sam}$) equipped with the MEA was then evaluated (Supporting Information, Experimental Section). A PEFC ($PEFC_{Ref}$) equipped with 20 wt% Pt/C (0.10 ± 0.01 $mg_{\text{-Pt}}\,cm^{-2}$) as the anode catalyst was also fabricated as a reference sample. Note that MEA anodes and cathodes are typically loaded with 0.1–0.4 $mg_{\text{-Pt}}\,cm^{-2}$ and 0.3–0.5 $mg_{\text{-Pt}}\,cm^{-2}$, respectively.[4,18] Figure 5 shows the current density (*j*) versus voltage (*V*), and *j* versus power density relationships for $PEFC_{Sam}$ and $PEFC_{Ref}$. The open circuit voltage of $PEFC_{Sam}$ (0.95 V) was 0.06 V smaller than that of $PEFC_{Ref}$. Additionally, the power density of $PEFC_{Sam}$ was also smaller than that of $PEFC_{Ref}$ when $j < 0.8\,A\,cm^{-2}$, but was larger when $j > 0.8\,A\,cm^{-2}$. The maximum power density of $PEFC_{Sam}$ was determined to be 487 $mW\,cm^{-2}$ at 1.2 $A\,cm^{-2}$, a value that was nearly identical to that of $PEFC_{Ref}$ (462 $mW\,cm^{-2}$ at 1.0 $A\,cm^{-2}$), which contained approximately five times more Pt anode catalyst. In combination, these results demonstrate that Pt-CTF has the potential to function as a cost-effective and efficient anode catalyst, as the amount of Pt required for catalytic activity is drastically lower than that of conventional Pt/C catalysts.

The electrode prepared with 2.8 wt% Pt-CTF exhibited superior electrocatalytic HOR activity compared to Pt/C (Figure 3a). The number of electrochemically active Pt atoms on Pt/C can be calculated from the electrical charge for the adsorption of upd-H in the CV, and was estimated to be $3.7 \times 10^{15}\,cm^{-2}$ for 20 wt% Pt/C. On the other hand, the total number of Pt atoms on 2.8 wt% Pt-CTF can be evaluated to be $4.3 \times 10^{15}\,cm^{-2}$ (Supporting Information, Note 1). Because a proportion of the Pt atoms on Pt-CTF were likely not exposed to the electrolyte and were therefore electrochemically inactive, the HOR activity per Pt atom on Pt-CTF was concluded to be equal to or more than that on Pt/C. The HOR can proceed by two different mechanisms on Pt: 1) the Heyrovsky–Volmer mechanism, by end-on adsorption of hydrogen molecules and, 2) the Tafel–Volmer mechanism, by bridge-type adsorption.[16] The dissociative adsorption of hydrogen molecules by bridge-type adsorption, which is the rate-determining step for HOR, is able to occur on single Pt atoms.[21] As comparable HOR activities were observed here between Pt-CTF and commercial 20 wt% Pt/C, we speculate that both mechanisms proceed on single Pt atoms.

Bulk Pt electrodes modified with a self-assembled patterned monolayer of calix[4]arene molecules were previously shown to have oxygen tolerance.[7] The adsorbed calix[4]arene molecules selectively blocked the ORR, whereas the HOR was able to proceed without suppression. The selectivity for these reactions is determined by the number of available Pt sites, with the HOR requiring significantly fewer sites compared to the ORR. Herein, reaction selectivity was achieved by loading Pt in an atomically dispersed form, thereby decreasing the total ORR activity without interfering with the HOR pathways. Using this novel strategy, we successfully obtained an oxygen-tolerant HOR anode loaded with a significantly reduced amount of Pt compared to conventional anodes and which may have practical application in PEFCs.

In conclusion, we demonstrated that 0.29 wt% Pt-CTF has superior electrocatalytic HOR activity without the requirement for an overpotential. Notably, Pt-CTF also exhibited high oxygen tolerance, which was attributed to the dispersion of single Pt atoms throughout the CTF substrate. Moreover, when the loading amount of Pt was increased to 2.8 wt%, the resulting electrode showed electrocatalytic HOR activity comparable to commercial 20 wt% Pt/C, a property that is of high practical importance for protecting PEFC cathodes from degradation during start-up/shut-down cycles. Furthermore, because the ORR catalytic activity of 2.8 wt% Pt-CTF was low due to the abundance of atomically dispersed Pt, the PEFC cathode would be protected from corrosive degradation. As various types of covalent organic frameworks other than CTF are available, and because metals other than Pt can be doped into such frameworks, we anticipate that the synthesis strategy reported here can be used to construct novel electrocatalytic materials with both high activity and selectivity.

Acknowledgements

This research was supported by the PRESTO Program of the Japan Science and Technology Agency (JST). Synchrotron radiation experiments were performed at the BL01B1 beamline of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; Proposal no. 2015A1302, 2015B1174, 2016A1120, 2016A1464). We thank Dr. T. Ina (JASRI) and Dr. G. Tei (Panasonic) for their technical support with the XAFS measurements and the fuel cell testing, respectively, and Prof. Dr. K. Uosaki (National Institute for Materials Science, Japan) for fruitful discussions.

Keywords: covalent triazine frameworks · electrocatalysis · fuel cells · platinum

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 13184–13188
Angew. Chem. **2016**, *128*, 13378–13382

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[1] a) K.-Y. Chan, J. Ding, J. Ren, S. Cheng, K. Y. Tsang, *J. Mater. Chem.* **2004**, *14*, 505–516; b) J. Baxter, Z. Bian, G. Chen, D. Danielson, M. S. Dresselhaus, A. G. Fedorov, T. S. Fisher, C. W. Jones, E. Maginn, U. Kortshagen, A. Manthriam, A. Nozik, D. R. Rolison, T. Sands, L. Shi, D. Sholl, Y. Wu, *Energy Environ. Sci.* **2009**, *2*, 559–588; c) S. Du, B. G. Pollet, *Int. J. Hydrogen Energy* **2012**, *37*, 17892–17898; d) K. Fugane, T. Mori, D. R. Ou, P. Yan, F. Ye, H. Yoshikawa, J. Drennan, *Langmuir* **2012**, *28*, 16692–16700.

[2] a) T. Saida, O. Sekizawa, N. Ishiguro, M. Hoshino, K. Uesugi, T. Uruga, S. Ohkoshi, T. Yokoyama, M. Tada, *Angew. Chem. Int. Ed.* **2012**, *51*, 10311–10314; *Angew. Chem.* **2012**, *124*, 10457–10460; b) T. Takeguchi, T. Yamanaka, K. Asakura, E. N. Muhamad, K. Uosaki, W. Ueda, *J. Am. Chem. Soc.* **2012**, *134*, 14508–14512.

[3] a) F. T. da Silva, V. A. Dalmazzo, M. R. Becker, M. O. Souza, E. M. A. Martini, *Ionics* **2014**, *20*, 381–388; b) C. V. Rao, B. Viswanathan, *J. Phys. Chem. C* **2010**, *114*, 8661–8667; c) D. Strmcnik, M. Uchimura, C. Wang, R. Subbaraman, N. Danilovic, D. Vliet, A. P. Paulikas, V. R. Stamenkovic, N. M. Markovic, *Nat. Chem.* **2013**, *5*, 300–306; d) X. Wang, R. K. Ahluwalia, A. J. Steinbach, *J. Electrochem. Soc.* **2013**, *160*, F251–F261; e) J. Durst, C. Simon, F. Hasché, H. A. Gasteiger, *J. Electrochem. Soc.* **2014**, *162*, F190–F203; f) E. Billy, F. Maillard, A. Morin, L. Guetaz, F. Emieuxa, C. Thurier, P. Doppelt, S. Donet, S. Mailley, *J. Power Sources* **2010**, *195*, 2737–2746.

[4] H. A. Gasteiger, S. S. Kocha, B. Sompalli, F. T. Wanger, *Appl. Catal. B* **2005**, *56*, 9–35.

[5] A. B. Suryamas, G. M. Anikumar, S. Sago, T. Ogi, K. Okuyama, *Catal. Commun.* **2013**, *33*, 11–14.

[6] a) C. A. Reiser, L. Bregoli, T. W. Patterson, J. S. Yi, J. D. Yang, M. L. Perry, T. D. Jarvi, *Electrochem. Solid-State Lett.* **2005**, *8*, A273–A276; b) B. Genorio, R. Subbaraman, D. Strmcnik, D. Tripkovic, V. R. Stamenkovic, N. M. Marković, *Angew. Chem. Int. Ed.* **2011**, *50*, 5468–5472; *Angew. Chem.* **2011**, *123*, 5582–5586; c) R. B. Kaspar, J. A. Wittkopf, M. D. Woodroof, M. J. Armstrong, Y. Yan, *J. Electrochem. Soc.* **2016**, *163*, F377–F383.

[7] B. Genorio, D. Strmcnik, R. Subbaraman, D. Tripkovic, G. Karapetrov, V. R. Stamenkovic, S. Pejovnik, N. M. Marković, *Nat. Mater.* **2010**, *9*, 998–1003.

[8] a) B. Qiao, A. Wang, X. Yang, L. F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li, T. Zhang, *Nat. Chem.* **2011**, *3*, 634–641; b) H. Wei, X. Liu, A. Wang, L. Zhang, B. Qiao, X. Yang, Y. Huang, S. Miao, J. Liu, T. Zhang, *Nat. Commun.* **2014**, *5*, 5634; c) M. Moses-DeBusk, M. Yoon, L. F. Allard, D. R. Mullins, Z. Wu, X. Yang, G. Veith, G. M. Stocks, C. K. Narula, *J. Am. Chem. Soc.* **2013**, *135*, 12634–12645.

[9] S. Yang, J. Kim, Y. J. Tak, A. Soon, H. Lee, *Angew. Chem. Int. Ed.* **2016**, *55*, 2058–2062; *Angew. Chem.* **2016**, *128*, 2098–2102.

[10] C. H. Choi, M. Kim, H. C. Kwon, S. J. Cho, S. Yun, H.-T. Kim, K. J. J. Mayrhofer, H. Kim, M. Choi, *Nat. Commun.* **2016**, *7*, 10922.

[11] K. Kamiya, R. Kamai, K. Hashimoto, S. Nakanishi, *Nat. Commun.* **2014**, *5*, 5040.

[12] a) K. Iwase, T. Yoshioka, S. Nakanishi, K. Hashimoto, K. Kamiya, *Angew. Chem. Int. Ed.* **2015**, *54*, 11068–11072; *Angew. Chem.* **2015**, *127*, 11220–11224; b) T. Yoshioka, K. Iwase, S. Nakanishi, K. Hashimoto, K. Kamiya, *J. Phys. Chem. C*, **2016**, *120*, 15729–15734.

[13] J. F. Llopis, F. Colom in *Encyclopedia of Electrochemistry of the Elements*, Vol. VI (Eds.: A. J. Bard), Marcel Dekker, New York, **1976**, p. 169.

[14] a) H. Ogasawara, M. Ito, *Chem. Phys. Lett.* **1994**, *221*, 213–218; b) N. M. Marković, B. M. Grgur, P. N. Ross, *J. Phys. Chem. B* **1997**, *101*, 5405–5413.

[15] K. Kinoshita, J. Lundquist, P. Stonehart, *J. Catal.* **1973**, *31*, 325–334.

[16] E. Skúlason, V. Tripkovic, M. E. Björketun, S. Gudmundsdóttir, G. Karlberg, J. Rossmeisl, T. Bligaard, H. Jónsson, J. K. Nørskov, *J. Phys. Chem. C* **2010**, *114*, 18182–18197.

[17] V. Tripkovic, M. Vanin, M. Karamad, M. E. Björketun, K. W. Jacobsen, K. S. Thygesen, J. Rossmeisl, *J. Phys. Chem. C* **2013**, *117*, 9187–9195.

[18] a) H. A. Gasteiger, J. E. Panels, S. G. Yan, *J. Power Sources* **2004**, *127*, 162–171; b) A. Pozio, R. F. Silva, M. Francesco, L. Giorgi, *Electrochim. Acta* **2003**, *48*, 1543–1549; c) Y.-H. Cho, J. W. Lim, Y. S. Kang, Y.-H. Cho, O.-H. Kim, N.-H. Kwon, O. J. Kwon, W.-S. Yoon, H. Choe, Y.-E. Sung, *Int. J. Hydrogen Energy* **2012**, *37*, 2490–2497; d) S. Litster, G. McLean, *J. Power Sources* **2004**, *130*, 61–76.

[19] C. H. Choi, H. C. Kwon, S. Yook, H. Shin, H. Kim, M. Choi, *J. Phys. Chem. C* **2014**, *118*, 30063–30070.

[20] a) H. S. Wroblowa, Y. C. Pan, G. J. Razumney, *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *69*, 195–201; b) A. J. Appleby, M. J. Savy, *J. Electroanal. Chem. Interfacial Electrochem.* **1978**, *92*, 15–30; c) J. C. Huang, R. K. Sen, E. Yeager, *J. Electrochem. Soc.* **1979**, *126*, 786–792.

[21] a) K. G. Dyall, *J. Chem. Phys.* **1993**, *98*, 9678–9686; b) B. Minaev, H. Ågren, *J. Mol. Catal. A* **1999**, *149*, 179–195; c) M. N. Huda, L. Kleinman, *Phys. Rev. B* **2006**, *74*, 195407.

Received: August 9, 2016
Revised: August 29, 2016