Nano-sized TiN on carbon black as an efficient electrocatalyst for the oxygen reduction reaction prepared using an mpg-C$_3$N$_4$ template†

Jia Chen,[a] Kazuhiro Takanabe,[a] Ryohji Ohnishi,[a] Daling Lu,[b] Saori Okada,[c] Haruna Hatasawa,[c] Hiroyuki Morioka,[c] Markus Antonietti,[d] Jun Kubota[a] and Kazunari Domen*[a]

The direct synthesis of TiN nanoparticles on carbon black (CB) was achieved using an mpg-C$_3$N$_4$/CB composite as a template. The obtained TiN/CB composites ensured improved contact between TiN and CB, functioning as an efficient cathode catalyst for oxygen reduction reaction (ORR) in polymer electrolyte fuel cells (PEFCs). The preparation procedure developed in this study is applicable for the synthesis of a variety of supported nano-nitride catalysts.
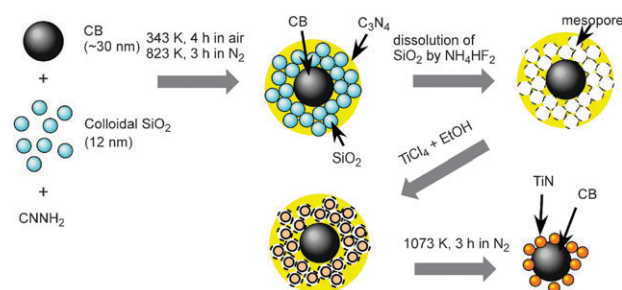
The polymer electrolyte fuel cell (PEFC) was developed as a clean power source for residences and vehicles because of its high energy-conversion efficiency, relatively low operating temperature, and high power density.[1] The performance of cathode catalysts for the oxygen reduction reaction (ORR) strongly limits the overall PEFC efficiency. Furthermore, a large amount of Pt or Pt–alloy nanoparticles are typically employed.[1] The use of such precious metals, which have limited reserves on the earth, prohibits the widespread commercialization of PEFCs.

Extensive studies of non-noble metal cathode catalysts have been performed, mainly employing Co-based or Fe-based catalysts, the stability of which is a major issue.[2] The active species are reported to be nitrogen-associated Co or Fe ions.[2] Another approach for non-noble metal cathodes is the use of carbo-oxy-nitrides (CNO) of IV and V transition metal catalysts, pioneered by Ota and co-workers.[3,4] These transition metal CNO species are expected to be highly tolerant to the oxidizing and acidic reaction conditions prevalent in PEFCs.[3] The onset potentials for the ORR on Zr-based and Ta-based catalysts were reportedly close to those of Pt-based catalysts.[3] Conventional synthesis of these catalysts, however, requires high-temperature treatment and produces bulky, low-surface-area catalysts, resulting in low current densities.

Certain nano-sized metal nitrides, on the other hand, have been successfully synthesized using nanoconfinement by a mesoporous graphite-like (mpg) C$_3$N$_4$ nitrogen source and template.[5] A variety of reactions could potentially be catalyzed at tremendous rates on these high surface area nano-nitrides. Handling of these nanoparticles is often difficult because they have a strong tendency to aggregate. Deposition of separated nanoparticles on the support materials can help maximize the nanoparticle surface area, leading to higher catalytic performance.

This study demonstrates that titanium nitride nanoparticles, prepared by structural replication from mpg-C$_3$N$_4$, showed efficient electrocatalytic activity for ORR. This is a common application for both nitride nanoparticles and non-noble-metal cathode catalysts. By dispersing the nanoparticles of metal nitrides, active for oxygen reduction, well on a conductive carbon substrate, catalytic activity can be coupled to the excellent electronic conductivity of the carbon material, and a high current density in fuel cell application can be expected. Such an approach would therefore solve both the problem of accessible catalyst-surface area as well as the combination of high catalytic activity with sufficient background conductivity. This study deals with nitrides of titanium to start with since it is stable in acidic medium and widely available and inexpensive, suitable for substituent of noble metals as the active component of the cathodes.

Scheme 1 illustrates the simplified preparation procedure developed in this study for highly-dispersed TiN supported on carbon black (CB). The CB support is not susceptible to fluoric acid, enabling the synthesis of an mpg-C$_3$N$_4$ coating on the CB particles, using colloidal silica as a template for the creation of mesopores. The BET surface area and pore volume of the mpg-C$_3$N$_4$/CB sample were 194 m^2 g^{-1} and 0.64 cm^3 g^{-1}, respectively (the pristine Vulcan CB values were 240 m^2 g^{-1}

[a] Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 300-1514, Japan. E-mail: domen@chemsys.t.u-tokyo.ac.jp; Fax: +81 3 5841 8838; Tel: +81 3 5841 1148
[b] Center for Advance Materials Analysis, Technical Department, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan
[c] Toppan Technical Research Institute, TOPPAN PRINTING Co., Ltd., 4-2-3 Takanodai-minami, Sugito-cho, Kitakatsushika-gun, Saitama, 345-8508, Japan. Fax: +81 480 33 9022
[d] Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Research Campus Golm, 14476 Potsdam, Germany. Fax: +49 331 567 9502
† Electronic supplementary information (ESI) available: Experimental and characterization details, Fig. S1–S4. See DOI: 10.1039/c0cc02048f

Scheme 1 Scheme showing the direct synthesis of mpg-C$_3$N$_4$ on carbon black (CB), followed by nano-TiN formation on CB.

and 0.32 cm^3 g^{-1}, respectively), and the average pore size was 12 nm (Fig. S1, ESI†), matching the diameter of the colloidal silica (12 nm). The direct synthesis of TiN nanoparticles using the mpg-C$_3$N$_4$ template ensured their high dispersion with good contact to the CB substrate while setting a controlled nanoparticle size by reaction in the pore.

The transmission electron microscope (TEM) images of TiN nanoparticles prepared with and without CB are shown in Fig. 1. TiN nanoparticles with a diameter of ∼4 nm form a polycrystalline aggregate, as confirmed by electron diffraction (Fig. 1 inset, left). The image (Fig. 1, right) of a sample prepared according to the method shown in Scheme 1 depicts the same TiN nanoparticles with a uniform size of ∼4 nm, however now highly dispersed on CB. The weight ratio of TiN/(TiN + CB) was estimated to be ∼6 wt% using thermo-gravimetry analysis, under the assumption that the remaining species was TiO$_2$ after complete combustion of the carbon support under flowing air up to 1173 K. The low loading, in combination with the small particle size, made it difficult to detect a clear peak of the Ti species on CB in X-ray diffraction (XRD, Fig. S2, ESI†), but the XRD of the corresponding Ti nanoparticles prepared using an mpg-C$_3$N$_4$ template without CB indicate clearly TiN formation (Fig. S2, ESI†), which is also the outcome expected from the literature.[5]

The prepared TiN/CB catalyst was examined for ORR in 0.1 M H$_2$SO$_4$ aq. at 303 K. A high cathodic current associated with the ORR was observed with an onset potential of 0.84 V vs. RHE (at 1 μA). The measured current (Fig. 2A–c) was much higher than those attained with TiN/CB catalysts prepared by impregnation on CB after TiN formation (Fig. 2A–a) or those prepared by physical mixing of mpg-C$_3$N$_4$ and CB followed by TiN formation (Fig. 2A–b). The difference is attributed to the better dispersion of TiN sites on CB, as evidenced by TEM images, while aggregation of TiN nano-particles cannot be avoided for the samples prepared without CB (Fig. S3, ESI†).

C$_3$N$_4$ is a semiconductor, exhibiting no activity for ORR, even when deposited on CB (Fig. 2B–g). C$_3$N$_4$/CB composite treated in flowing N$_2$ at 1073 K (Fig. 2B–e) showed higher ORR activity than non-treated CB (Fig. 2B–f), which is consistent with a report that N-doped carbon showed moderate ORR activity.[6] TiN/CB had a much higher onset potential (activity per site) and current (the number of active sites) than these other combinations (Fig. 2B). Therefore, highly-dispersed
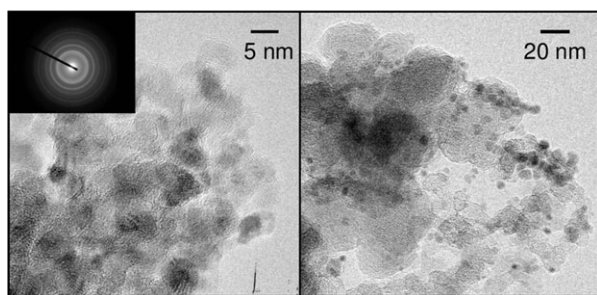

Fig. 1 TEM image and electron diffraction pattern of TiN nano-particle aggregates prepared without CB (left), and of a TiN/CB sample prepared according to Scheme 1 (right).
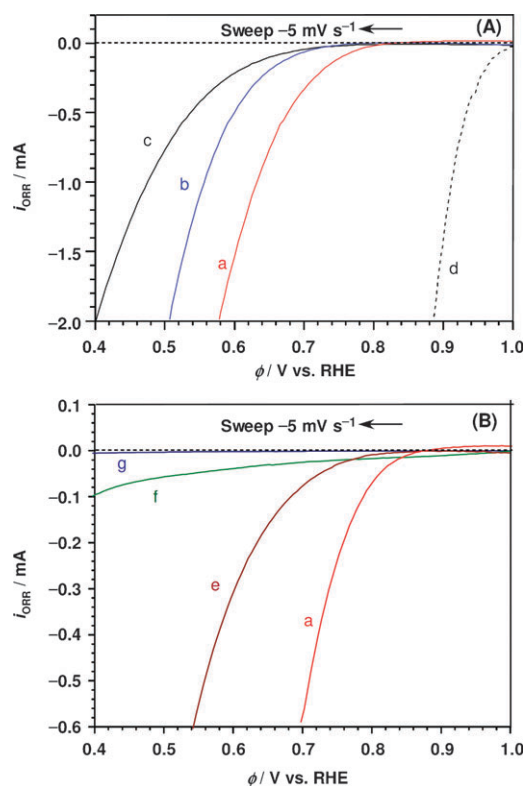

Fig. 2 Voltammograms for the ORR on various TiN/CB, the related samples and Pt/CB in 0.1 M H$_2$SO$_4$ at 303 K. (a) A sample prepared by mpg-C$_3$N$_4$ synthesis on CB, followed by TiN formation; (b) a sample prepared by impregnation of C$_3$N$_4$ on CB, followed by TiN formation; (c) a sample prepared by impregnation of TiN nanoparticles on CB; (d) Pt/CB; (e) C$_3$N$_4$-treated CB; (f) CB only; (g) C$_3$N$_4$ only.

TiN nanoparticles can be associated with active sites for ORR, and were more active than the previously-reported N-doped carbon.[6] The TiN/CB sample showed constant ORR perfor-mance during 1000 cycles of charging–discharging treatments between 0.6–1.0 V vs. RHE under N$_2$ atmosphere, indicative of high durability of the materials as cathode catalysts, as shown in Fig. S4 (ESI†).

A power generation test using a single cell containing these TiN/CB as a cathode was carried out, and the results are shown in Fig. 3. A high open circuit voltage (OCV) of 0.85 V, and maximum power densities of 70 and 208 mW cm^{-2} were attained under back-pressures of 0 and 0.3 MPa, respectively. This was comparable to the highest performance reported for PEFCs based on a non-noble metal cathode. The current at 0.6 V under no back-pressure remained almost constant for 100 h after an initial drop in the current (Fig. S5, ESI†). These results indicate that the nano-TiN/CB catalyst is stable and very promising as a non-noble-metal cathode using nitrides of IV and V group metal.

In conclusion, our preparation method generated uniform nano-sized nitrides (TiN), well-dispersed on a carbon support. The nano-TiN on CB exhibited excellent ORR perfor-mance with improved ORR current. The preparation method developed in this study can be applied to nitride formation with other elements, which is expected to lead to even improved ORR activity (onset potential). Moreover, this study also opens the potential to apply these supported nitrides as
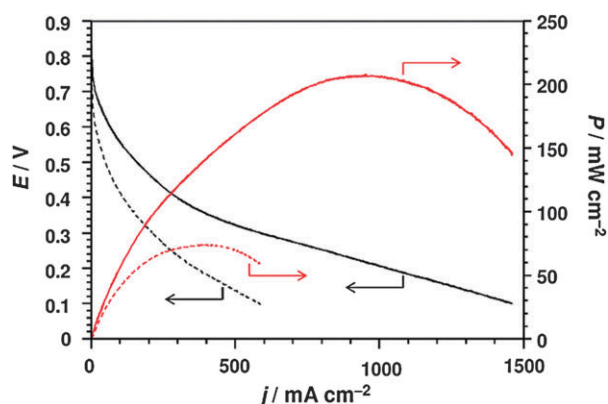
Fig. 3 Current–voltage and current–power curves of a single cell. The cathode and anode catalysts were TiN/CB and Pt/CB, respectively. The temperature of the entire cell was maintained at 363 K and H$_2$ (anode) and O$_2$ (cathode) flows, humidified at 363 K under backpressures of 0 (dashed lines) and 0.3 MPa (solid lines), were used. For further details, see the ESI.†

efficient catalysts for a variety of reactions, as supported nano-nitrides are by nature close to noble metals.

Notes and references

1 (a) L. Carrette, K. A. Friedrich and U. Stimming, *Fuel Cells*, 2001, **1**, 5; (b) M. Z. Jacobson, W. G. Colella and D. M. Golden, *Science*, 2005, **308**, 1901.

2 (a) F. Jaouen, J. Herranz, M. Lefèvre, J.-P. Dodelet, U. I. Kramm, I. Herrmann, P. Bongandoff, J. Maruyama, T. Nagaoka, A. Garsuch, J. R. Dahn, T. Olson, S. Pylypenko, P. Atanassov and E. A. Ustinov, *ACS Appl. Mater. Interfaces*, 2009, **1**, 1623; (b) C. W. B. Bezerra, L. Zhang, K. Lee, H. Liu, A. L. B. Marques, E. P. Marques, H. Wang and J. Zhang, *Electrochim. Acta*, 2008, **53**, 4937; (c) R. Bashyam and P. Zelenay, *Nature*, 2006, **443**, 63; (d) U. I. Koslowski, I. Abs-Wurmabach, S. Fiechter and P. Bogdanoff, *J. Phys. Chem. C*, 2008, **112**, 15356; (e) J. M. Ziegelbauer, T. S. Olson, S. Phylypenko, F. Alamgir, C. Jaye, P. Atanassov and S. Mukerjee, *J. Phys. Chem. C*, 2008, **112**, 8839; (f) T. Schilling and M. Bron, *Electrochim. Acta*, 2008, **53**, 5379; (g) M. Yuasa, A. Yamaguchi, H. Itsuki, K. Tanaka, M. Yamamoto and K. Oyaizu, *Chem. Mater.*, 2005, **17**, 4278; (h) N. P. Subramanian, S. P. Kumaraguru, H. Colon-Mercado, H. Kim, B. N. Popov, T. Black and D. A. Chen, *J. Power Sources*, 2006, **157**, 56; (i) A. H. C. Sirk, S. A. Campbell and V. I. Birss, *J. Electrochem. Soc.*, 2008, **155**, B592; (j) V. Nallathambi, J.-W. Lee, S. P. Kumaraguru, G. Wu and B. N. Popov, *J. Power Sources*, 2008, **183**, 34; (k) J. Maruyama, N. Fukui, M. Kawaguchi and I. Abe, *J. Power Sources*, 2008, **182**, 489; (l) M. Lefèvre, E. Proietti, F. Jaouen and J.-P. Dodelet, *Science*, 2009, **324**, 71; (m) T. E. Wood, Z. Tan, A. K. Schmoeckel, D. O'Neill and R. Atanasoski, *J. Power Sources*, 2008, **178**, 510; (n) B. Wang, *J. Power Sources*, 2005, **152**, 1.

3 (a) A. Ishihara, K. Lee, S. Doi, S. Mitsushima, N. Kamiya, M. Hara, K. Domen, K. Fukuda and K. Ota, *Electrochem. Solid-State Lett.*, 2005, **8**, A201; (b) S. Doi, A. Ishihara, S. Mitsushima, N. Kamiya and K. Ota, *J. Electrochem. Soc.*, 2007, **154**, B362; (c) J.-H. Kim, A. Ishihara, S. Mitsushima, N. Kamiya and K. Ota, *Electrochim. Acta*, 2007, **52**, 2492.

4 (a) R. Ohnishi, Y. Takahashi, A. Takagaki, J. Kubota and K. Domen, *Chem. Lett.*, 2008, **37**, 838; (b) A. Takagaki, Y. Takahashi, F. Yin, K. Takanabe, J. Kubota and K. Domen, *J. Electrochem. Soc.*, 2009, **156**, B811; (c) F. Yin, K. Takanabe, J. Kubota and K. Domen, *J. Electrochem. Soc.*, 2010, **157**, B240; (d) R. Ohnishi, M. Katayama, K. Takanabe, J. Kubota and K. Domen, *Electrochim. Acta*, 2010, **55**, 5393.

5 (a) A. Fischer, J. O. Müller, M. Antonietti and A. Thomas, *ACS Nano*, 2008, **2**, 2489; (b) A. Fischer, M. Antonietti and A. Thomas, *Adv. Mater.*, 2007, **19**, 264; (c) Y.-S. Jun, W. H. Hong, M. Antonietti and A. Thomas, *Adv. Mater.*, 2009, **21**, 4270; (d) A. Thomas, F. Goettmann and M. Antonietti, *Chem. Mater.*, 2008, **20**, 738; (e) A. Fischer, Y.-S. Jun, A. Thomas and M. Antonietti, *Chem. Mater.*, 2008, **20**, 7383.

6 (a) H. Niwa, K. Horiba, Y. Harada, M. Oshima, T. Ikeda, K. Terakura, J. Ozaki and S. Miyata, *J. Power Sources*, 2009, **187**, 93; (b) S. M. Lyth, Y. Nabae, S. Moriya, S. Kuroki, M. Kakimoto, J. Ozaki and S. Miyata, *J. Phys. Chem. C*, 2009, **113**, 20148; (c) K. Gong, F. Du, Z. Xia, M. Durstock and L. Dai, *Science*, 2009, **323**, 760.