

Surface-regulated nano-SnO₂/Pt₃Co/C cathode catalysts for polymer electrolyte fuel cells prepared by a new Sn deposition method

The development of next-generation polymer electrolyte fuel cells (PEFCs) with high performance and durable cathode catalysts under harsh PEFC operating conditions is indispensable for the widespread commercialization of PEFC vehicles. Various Pt-M alloy/C catalysts have been studied as promising cathode catalysts and considerable effort has been devoted to the fabrication of Pt-Co nanostructures with higher oxygen reduction reaction (ORR) activity and longer-term durability than Pt/C. On the other hand, Pt/C cathode catalysts have been modified by metal oxides to change the redox behavior and improve the ORR activity of Pt nanoparticles. We succeeded in preparing a SnO₂-modified Pt₃Sn/C cathode catalyst with better ORR performance than a Pt/C catalyst [1]. Recently, we have found a new way to fabricate surface-regulated SnO₂/Pt₃Co/C cathode catalysts with SnO₂ nanoislands on a Pt skeleton-skin surface with compressive strain and defects/dislocations on Pt₃Co nanoparticle cores. These catalysts were much more active than expected from the d-band center values [2]. The structural arrangement also created two different reaction sites (Site 1 at the Pt skin surface and the more active Site 2 at the nano-SnO₂ periphery) in a tunable mode with different Pt/Sn ratios. The SnO₂/Pt₃Co/C cathode catalysts were characterized by *in situ* XAFS, XPS, XRD, and TEM/STEM-EDS.

A series of SnO₂/Pt₃Co/C catalysts with Pt/Sn= 4/1, 9/1, 11/1, and 15/1 were prepared by a new selective Sn deposition method while regulating the electrochemical potential at -0.45 V vs AgCl in 0.1 M HClO₄. We found that at this potential, Sn deposition selectively occurs on the Pt surfaces and the Sn deposition on the carbon support can be neglected. The deposited Sn species were identified as SnO₂ nanoislands by XANES, XPS, and STEM-EDS [2].

Figures 1(a) and 1(c) are HR-TEM images of the Pt₃Co/C and SnO₂/Pt₃Co/C (Pt/Sn=9/1) catalysts, respectively [2]. The lattice contrast profiles of Fig. 1(b) along the red and blue arrows in Fig. 1(a) for a Pt₃Co/C particle revealed the regular Pt₃Co interplane distance for the Pt₃Co core and the Pt interplane distances for three Pt surface layers. The HR-TEM image for the SnO₂/Pt₃Co/C with Pt/Sn=9/1 after aging in Fig. 1(c) showed that the Pt-enriched surface possessed many atomic defects and dislocations, with typical ones indicated by yellow arrows. The lattice contrast profiles in Fig. 1(d) along the red, blue, and green arrows near the defects and dislocations (a-e) in Fig. 1(c) showed irregular intensities and intervals, which is evidence for a rough/skeleton surface morphology at the Pt surface layers. The atomic arrangements indicated compressive strain at the Pt surface layers due to the effect of the underlying Pt₃Co core structure. Figures 1(e) and 1(f) are a TEM

image of the SnO₂/Pt₃Co/C catalyst (Pt/Sn=9/1) and EDS line profiles showing the Pt-enriched surface with SnO₂ nanoislands, respectively.

The ORR activities of the fabricated cathode catalysts were estimated by linear sweep voltammetry (LSV) at 0.9 V_{RHE}, and the mass activities (MAs) and surface specific activities (SAs) were estimated using Koutecky-Levich plots calculated from the LSV curves [2]. The MA of Pt₃Co/C was 2.2 times larger than that of Pt/C, and both values were within the MA values in the literature. Note that the MA of Pt₃Co/C was further increased by a factor 2.4 by the addition of SnO₂ (Pt/Sn=9/1). Thus,

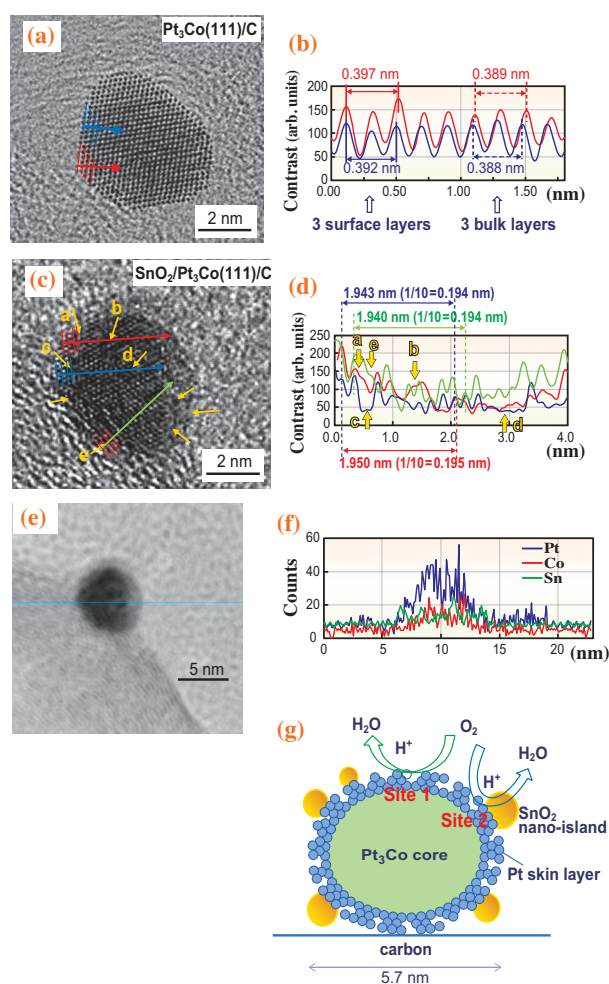


Fig. 1. (a) Atomic arrangement of Pt₃Co(111) plane in a TEM image of Pt₃Co/C after aging. (b) Lattice contrast profiles for the interplane distances along the red and blue arrows in (a). (c) Atomic arrangement of Pt₃Co(111) plane in a TEM image of SnO₂/Pt₃Co/C (Pt/Sn=9/1) after aging. Yellow arrows show typical defects and dislocations. (d) Lattice contrast profiles for the interplane distances along the red and blue arrows in (c). (e) TEM image of the SnO₂/Pt₃Co/C catalyst (Pt/Sn=9/1) and (f) EDS line profiles for Pt (blue), Co (red), and Sn (green) along the light blue line in the TEM image. (g) Model structure and proposed ORR sites for the nano-SnO₂-decorated Pt₃Co/C catalyst with a Pt skeleton surface with compressive strain and defects/dislocations. [2]

the MA of the SnO₂/Pt₃Co/C catalyst (Pt/Sn=9/1) was 5.4 times larger than that of the Pt/C catalyst. This advantage of the SnO₂/Pt₃Co/C catalyst (Pt/Sn=9/1) was also maintained after 5,000 load cycles, where the MA of SnO₂/Pt₃Co/C was 7.8 times larger than that of Pt/C, showing the high durability of SnO₂/Pt₃Co/C. There was an optimum amount of SnO₂ for improving the ORR and durability. The SA of SnO₂/Pt₃Co/C with Pt/Sn=11/1 after 5,000 load cycles was 5.0 times larger than that of Pt/C. However, the SA in the case of Pt/Sn=4/1 decreased almost linearly with increasing number of load cycles. Thus, the MA and SA of the SnO₂/Pt₃Co/C catalysts are highest around Pt/Sn=9-11/1 [2].

The SAs of the catalysts were plotted against the CO stripping peak potential in Fig. 2(a) and changed as follows: Pt/C < Pt₃Co/C < SnO₂/Pt₃Co/C (Pt/Sn=15/1) < SnO₂/Pt₃Co/C (Pt/Sn=11/1) > SnO₂/Pt₃Co/C (Pt/Sn=9/1) > SnO₂/Pt₃Co/C (Pt/Sn=4/1), resulting in a volcano-shaped relationship between the CO stripping peak potential (relative d-band center) and the SA. The SAs of Pt-alloy catalysts have also been demonstrated to reveal a volcano-shaped relationship with the d-band center energy, as shown in the green dotted line in Fig. 2(a), where the two values reported in the literature for each of Pt/C (1), Pt₃Ni/C (2), Pt₃Co/C (3), Pt₃Fe/C (4), Pt₃V/C (5), and Pt₃Ti/C (6) were averaged and the values for Pt₃Co/C and Pt/C were normalized to the CO stripping peak potentials, respectively measured in this study [2]. Thus, the nano-SnO₂ in SnO₂/Pt₃Co/C with compressive strain at the Pt skeleton surface layers electronically modified the 5d level to decrease the d-band center, which led to weaker oxygen adsorption and improvement of the ORR. However, the same d-band center value did not show the same ORR activity (Fig. 2(a)), which indicates the existence of another factor promoting the ORR in the case of SnO₂/Pt₃Co/C catalysts in addition to the appropriate adjustment of the d-band center at the Pt surface sites (Site 1). Additional CO stripping peaks at much lower potentials (700-800 mV) appeared with the nano-SnO₂-decorated catalysts, which are regarded as being due to events at new surface sites (Site 2) [2]. We propose that the peripheral sites of the SnO₂ nanoislands with proton affinity at the Pt skeleton surface may provide these lower potential CO stripping sites and hence new ORR sites (Site 2 in Fig. 1(g)) for more weakly adsorbed O₂, facilitating the H⁺-O₂ interaction [2].

To obtain electronic and structural information on the nano-SnO₂/Pt₃Co/C catalysts, we conducted *in situ* XAFS measurements of RDE in 0.1 M HClO₄ by using a laboratory-built *in situ* XAFS cell at BL36XU [2]. Figure 2(b) shows the peak heights of the white lines (2p → 5d) in the *in situ* Pt L_{III}-edge XANES spectra of Pt/C, Pt₃Co/C, and SnO₂/Pt₃Co/C under stepwise changes in the potential at the RDE in 0.1 M HClO₄. In the potential gain process, the catalysts showed an increase in the white-line intensity above 0.8 V_{RHE}, indicating a positive charge of the Pt surfaces due to Pt-O bonding. During the

decrease in potential from 1.0 V_{RHE} to 0.4 V_{RHE} the white-line responses for the Pt/C and Pt₃Co/C did not retrace those in the potential gain process, showing a clear hysteresis [3]. It is notable that the nano-SnO₂/Pt₃Co/C exhibited no hysteresis in the potential operation between 0.4 and 1.0 V_{RHE}. Oxygen species adsorbed on the SnO₂/Pt₃Co/C surface at 1.0 V_{RHE} are readily reduced below 1.0 V_{RHE}, resulting in higher ORR performance [2].

In conclusion, the significant improvements in the ORR activity and durability were achieved with new nano-SnO₂/Pt₃Co/C catalysts, which were regulated by a strategic fabrication using a new selective electrochemical Sn deposition method and subsequent chemical treatments. The nano-SnO₂/Pt₃Co/C catalysts possessed a Pt₃Co core/Pt skeleton-skin structure decorated with SnO₂ nanoislands at the surface. Their high performances originated from the unique reactive periphery of the SnO₂ nanoislands at the compressive Pt surface with defects and dislocations. The present results provide a new insight into the development of a new class of next-generation PEFC cathode catalysts [2].

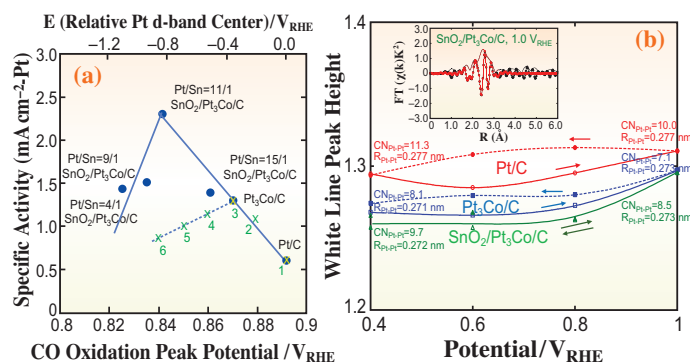


Fig. 2. (a) Relationship between the SAs and CO stripping peak potentials for SnO₂/Pt₃Co/C (Pt/Sn=4/1, 9/1, 11/1, and 15/1), Pt₃Co/C, and Pt/C (see [2]). (b) White-line peak heights in the *in situ* XANES spectra for Pt/C (red), Pt₃Co/C (blue), and SnO₂/Pt₃Co/C with Pt/Sn=11/1 (green) in the potential gain and decrease processes every 0.2 V between 0.4 and 1.0 V_{RHE}. Inset: results of EXAFS Fourier transform and curve fitting for SnO₂/Pt₃Co/C (Pt/Sn=11/1) at 1.0 V_{RHE}. [2]

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