



Short communication

Oxygen reduction catalytic ability of platinum nanoparticles prepared by room-temperature ionic liquid-sputtering method

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ABSTRACT

Pt nanoparticles can be produced by a Pt sputtering method onto trimethyl-*n*-propylammonium bis((trifluoromethyl)sulfonyl)amide ($\text{Me}_3\text{PrNTf}_2\text{N}$) room-temperature ionic liquid (RTIL) without stabilizing agents. Pt nanoparticles obtained by the Pt sputtering method showed mean particle size of ca. 2.3–2.4 nm independently of sputtering time. A Pt-embedded glassy carbon electrode (Pt-GCE) consisting of the Pt-sputtered RTIL and a glassy carbon plate showed a favorable catalytic activity to oxygen reduction reaction. The catalytic ability was enhanced by $\text{Me}_3\text{PrNTf}_2\text{N}$ modification of the Pt-GCE. In addition, carbon monoxide never absorbed onto the RTIL-modified Pt-GCE.

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1. Introduction

Room-temperature ionic liquid (RTIL), which is taken as synonymous with room-temperature molten salts and ambient-temperature molten salts, is currently known as a novel solvent because most RTILs have anomalous physicochemical properties such as negligible vapor pressure, wide electrochemical window, high thermal and radiochemical stability [1–3]. Before 1992, historical RTIL studies in energy and material sciences usually employed chloroaluminate RTILs, e.g., AlCl_3 -1-ethyl-3-methylimidazolium chloride (EtMelmCl) and AlCl_3 -1-(1-butyl)pyridinium chloride (BuPyCl), which have strong corrosive and hydroscopic nature, especially Lewis acidic ones with slight vapor pressure at the temperature over 373 K [4]. Therefore the researches must be conducted in an inert gas filled glove box or closed cell. However, birth of non-chloroaluminate RTILs drastically changed the situation

[5,6]. A great number of applications to energy and material sciences have been proposed and new technologies have been created by using recent non-chloroaluminate RTILs because of their anomalous features described above. In particular, vacuum technology using the RTIL systems will be one of next-generation technologies. Those are XPS techniques with RTILs [7–9], electron microscope technology with RTILs [9–13], metal sputtering onto RTILs [14–19] and so on.

Platinum possesses inherently a high catalytic activity for electrochemical oxygen reduction reaction (ORR). Further enhancement of Pt catalytic activity is one of the keys for practical application of PEM fuel cell systems because abundance of Pt on the planet is finite. Various preparation processes on novel Pt catalysts have been reported. There are some interesting articles that RTIL-modified Pt or Au nanoparticles show a good catalytic activity toward O_2 reduction [20–24]. Recently we have also succeeded to synthesize Pt nanoparticles having ca. 2–4 nm in diameter by the use of a RTIL-sputtering method and to prepare the electrode with the Pt nanoparticles for ORR [19].

In this article, we report a catalytic activity of the electrode with the Pt nanoparticles prepared by a RTIL-sputtering method toward the ORR. The purpose of this study is to clarify the catalytic activity of the Pt nanoparticles per unit area and to improve the characteristics of the Pt-embedded electrode.

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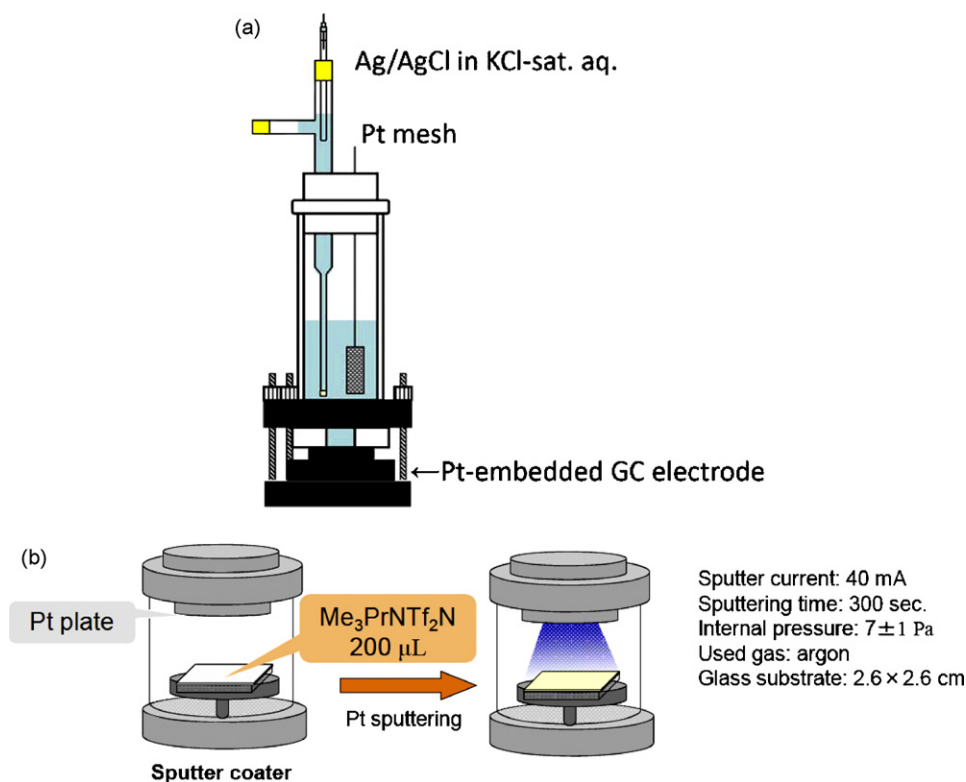


Fig. 1. Illustrations of (a) an electrochemical cell using the Pt-GCE and (b) a Pt nanoparticle synthesis by a RTIL-sputtering method.

2. Experimental

2.1. Preparation of Pt nanoparticles

The RTIL used for the preparation of Pt nanoparticles was trimethyl-*n*-propylammonium bis((trifluoromethyl)sulfonyl)-amide, Me₃PrNTf₂N (Kanto Chemical Co. Inc., ultrapure grade), which was dried in vacuum prior to use. We could not detect any impurities in the RTIL by using electrochemical method. A soda glass plate (2.5 cm × 2.5 cm), on which Me₃PrNTf₂N (0.2 mL) was spread, was set in a Cressington108 auto SE sputter coater. A Pt foil target (Ø 5.7 cm, 99.98%) was placed on 4.5 cm above the glass plate. Sputter deposition onto RTIL was conducted with sputter current of 40 mA in dry Ar (99.999%) atmosphere whose pressure did not exceed 7 ± 1 Pa. The sputtering was conducted at room temperature (298 ± 2 K).

2.2. Measurements and analyses

Size distribution of Pt nanoparticles was estimated by a Hitachi H-7650 transmission electron microscope (TEM) operated at 100 kV. Before the TEM observation, sample grids were prepared by dropping the sputtered RTIL onto a TEM grid (Ø 3.0 mm, copper, 400 mesh) with amorphous carbon thin layer. Elemental analysis was performed with an EDAX Genesis-XM2 energy dispersive X-ray (EDX) spectrometer and a Rigaku ZSX100e X-ray fluorescence (XRF) spectrometer. Surface condition analysis of the Pt nanoparticle-embedded glassy carbon electrode (Pt-GCE) was carried out by using a PerkinElmer Spectrum 100 FT-IR spectrometer with an attenuated total reflectance unit.

Electrocatalytic activities for Pt nanoparticles prepared in this investigation toward O₂ reduction were examined with an ALS Model 660A potentiostat/galvanostat controlled with a desktop computer and a three-electrode cell depicted in Fig. 1. The work-

ing electrode was a Pt-GCE, which was set at the bottom of the cell and sandwiched in between glass parts with an O-ring. A Pt mesh was used as the counter electrode. The Ag/AgCl electrode immersed in a KCl-saturated solution was employed as the reference electrode. All potential values are reported with respect to normal hydrogen electrode (NHE). The Pt-GCE was prepared by the following procedures: (i) heat treatment of the Pt-sputtered RTIL on a glassy carbon (GC) plate (2.5 cm × 2.5 cm) at various temperatures under atmospheric conditions; (ii) immersing the glassy carbon plate with 1.67 M KOH *iso*-propanolic solution for 12 h or rinsing the plate with dry acetonitrile; (iii) drying the resulting electrode under vacuum for 30 min prior to use. The heat treatment was conducted with a Koyo Thermo Systems REX-C900. If *iso*-propanolic solution was employed for the (ii), the glassy carbon plate was rinsed with nitric acid and ultrapure water before the drying process. Active surface area of the Pt-GCE was determined with amount of adsorbed carbon monoxide (CO) (GL Sciences, 99.9%) that was estimated by reference to previous reports [25,26]. The CO poisoning was electrochemically conducted by a constant potential method at +0.3 V (vs. NHE) for 40 min in CO-saturated 0.5 M H₂SO₄ aqueous solution. The resulting Pt-GCE was pretreated with multiple potential scans between 0 and +1.2 V (vs. NHE) under dry N₂ condition before oxygen reduction experiments in 0.5 M H₂SO₄ aqueous solution. The 0.5 M H₂SO₄ solution was deaerated with oxygen gas (99.999%) for more than 30 min.

3. Results and discussion

3.1. Preparation of Pt nanoparticles

Pt nanoparticles can be produced by a Pt sputtering method onto Me₃PrNTf₂N RTIL without any stabilizing agent [19]. This simple process can reproducibly yield Pt nanoparticles. Fig. 2 depicts

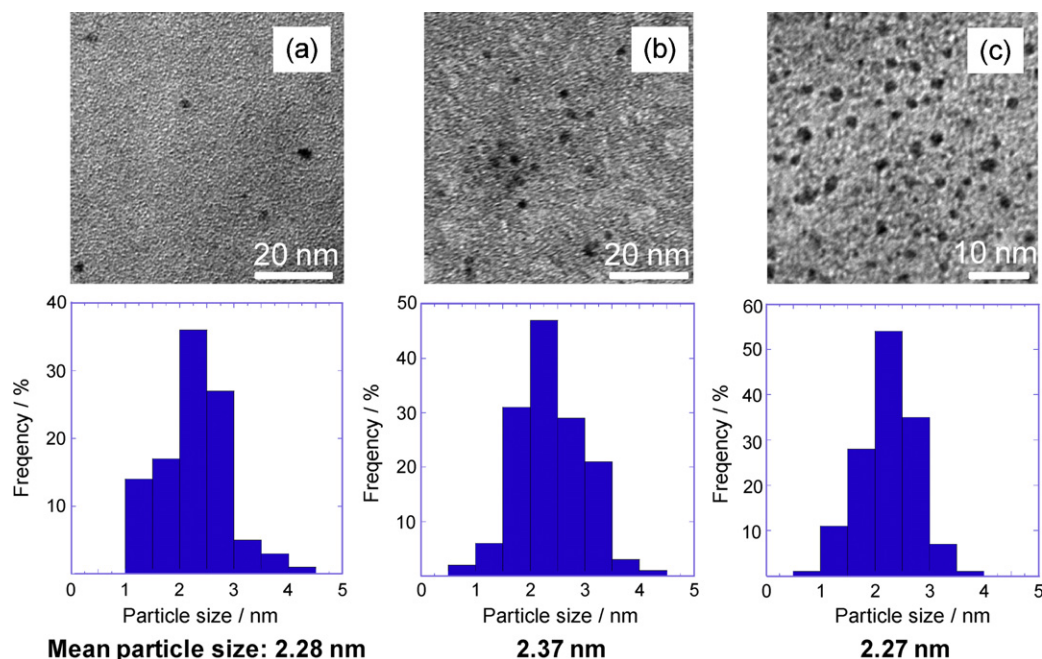


Fig. 2. TEM images and their size distribution diagrams at different sputtering time: (a) 300 s, (b) 900 s, and (c) 1800 s.

TEM images of Pt nanoparticles obtained by the Pt sputtering onto $\text{Me}_3\text{PrNTf}_2\text{N}$ at different sputtering times and their size distribution diagrams constructed from the TEM images. All the Pt nanoparticles have mean particle size of ca. 2.3–2.4 nm, and the particle size was of little relevance to the sputtering time. But the Pt concentration in the sputtered RTILs linearly increased with increasing the sputtering time. It is known that these Pt nanoparticles become slightly large after heat treatment exceeding 423 K [19]. The mean particle size (ca. 3.7 ± 0.1 nm) is substantially constant value independently of the heat temperature if the heat temperature is 423–573 K. 573 K was chosen as the maximum heat temperature to avoid pyrolysis of the RTIL. In this investigation, based on the report, heat treatment was carried out at 473–573 K so as to prepare a Pt nanoparticle-embedded glassy carbon electrode (Pt-GCE) because catalyst efficiency of Pt nanoparticle reaches the maximum at 4.0 nm in diameter [27].

3.2. ORR on Pt-GCEs

Very recently we have reported that Pt-GCE shows a favorable catalytic activity for ORR in 0.5 M H_2SO_4 aqueous solution [19]. But unfortunately it did not include important information on the surface condition of Pt nanoparticles on the Pt-GCE and on the catalytic ability of the Pt nanoparticles per unit area. The former was examined with infrared reflection absorption spectroscopy, and the latter was determined by a common electrochemical method. Fig. 3(a) and (b) indicate infrared reflection spectra for pure $\text{Me}_3\text{PrNTf}_2\text{N}$ and Pt-GCE rinsed with 1.67 M KOH *iso*-propanolic solution. After rinsing the Pt-GCE, there was no peak related to the RTIL, i.e., bare Pt surface appeared.

In order to determine active surface area of the Pt nanoparticles on the Pt-GCE, carbon monoxide, CO, stripping voltammetry was conducted. Steady-state cyclic voltammograms recorded at CO-absorbed Pt-GCEs are shown in Fig. 4(a)–(c). These Pt-GCEs were prepared at 473, 523, and 573 K. At first cycle, in all figures, an obvious oxidation wave corresponding to CO stripping appears at 0.8–0.9 V, and the wave completely disappears at sec-

ond cycle. The CO stripping wave becomes large with increasing the heat temperature for the Pt-embedded process. The Pt areas at the heat temperature of 473, 523, and 573 K were 0.031, 0.100, and $0.200 \text{ cm}^2\text{-Pt}$, respectively. Catalytic activity of these Pt-GCEs was examined by cyclic voltammetry in O_2 -saturated H_2SO_4 aqueous solution. The observed current densities were based on the active surface area of the Pt nanoparticles. In each case, a distinct reduction wave for ORR appeared (Fig. 5). What is interesting is that the catalytic activity per unit area was enhanced at lower heat treatment temperature. In fact, we expected an opposite result; that is, the catalytic activity per unit area increases as the Pt-embedded temperature increases because our previous result was that the

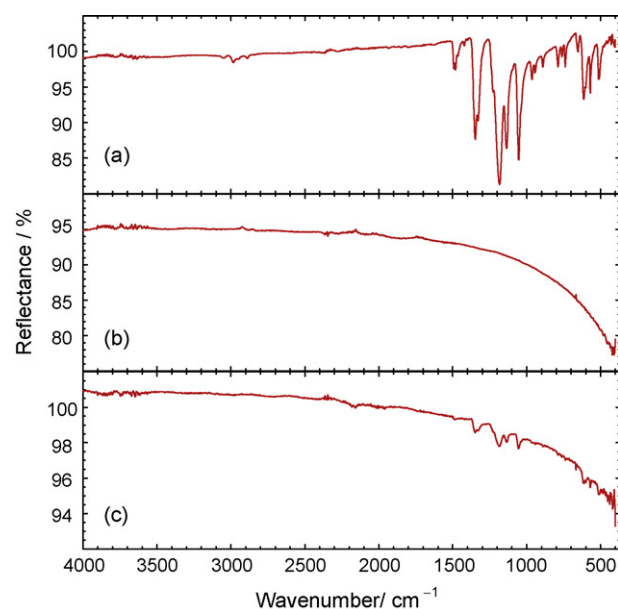


Fig. 3. Reflective FT-IR spectra of Pt-GCE prepared at 573 K: (a) $\text{MePrNTf}_2\text{N}$ on GC without heat treatment; (b) Pt-GCE rinsed with KOH *iso*-propanolic solution and nitric acid; (c) Pt-GCE rinsed with acetonitrile.

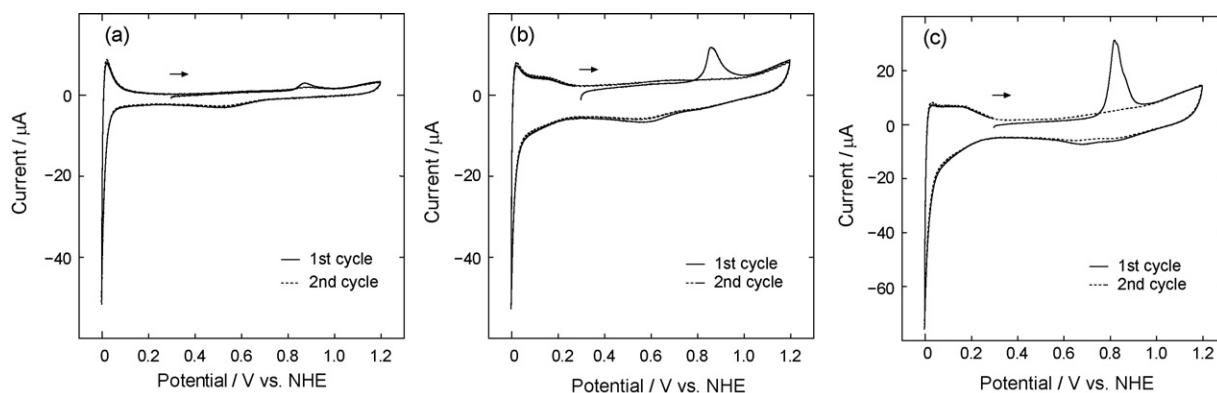


Fig. 4. Cyclic voltammograms recorded at Pt-GCEs, on which CO monolayer was absorbed. The heat temperatures for the Pt-GCE preparation were (a) 473 K, (b) 523 K, and (c) 573 K. The electrolyte was 0.5 M H₂SO₄ aqueous solution at 298 K. The scan rate was 10 mV s⁻¹.

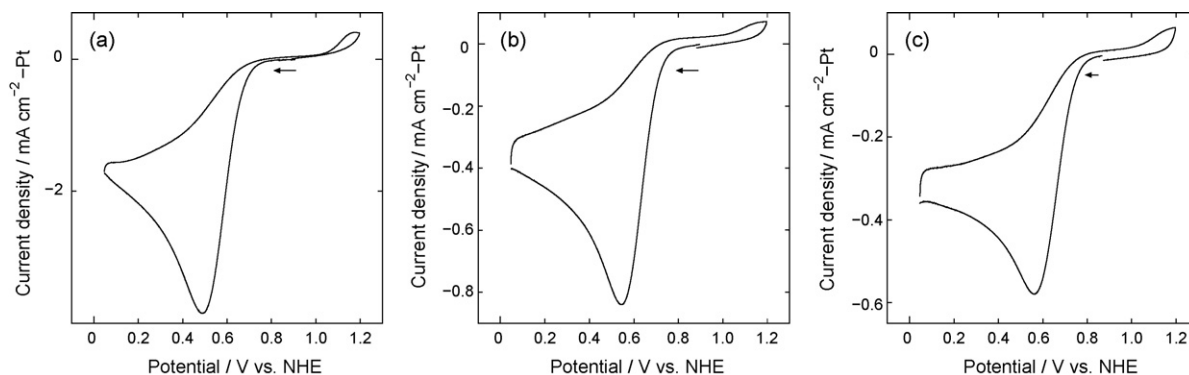


Fig. 5. Cyclic voltammograms recorded at Pt-GCEs in O₂-saturated 0.5 M H₂SO₄ aqueous solution at 298 K. The heat temperatures for the Pt-GCE preparation were (a) 473 K, (b) 523 K, and (c) 573 K. The scan rate was 10 mV s⁻¹.

reduction current for ORR increased at higher heat treatment temperature [19]. To understand this unexpected result precisely, surface morphology of these electrodes was observed by SEM. Fig. 6 exhibits typical SEM images at various Pt-embedded temperatures. Here, bright moiety should be Pt since Pt nanoparticles can release more secondary electrons than the glassy carbon plate. SEM images obviously whiten as the Pt-embedded temperature increases, i.e., amount of embedded Pt nanoparticles increases with the temperature. Therefore, increment in apparent reduction current for ORR should be caused by increase in Pt nanoparticles embedded on the GC. However, as shown in Fig. 5, the catalytic activity per unit area for the ORR becomes small at higher Pt-embedded temperature. It is highly likely that effective Pt surface area decreases if the Pt-embedded temperature increases because a dense Pt nanoparticle layer is formed on GC at higher temperature (Fig. 6). At this moment, due to lack of data on total weight of Pt nanoparticle embedded

on GC electrode, we cannot give the data on optimization of Pt-embedded condition to meet both higher current for the ORR per unit weight and higher catalytic activity of the Pt nanoparticles per unit area but we will report it in the near future.

3.3. ORR on RTIL-modified Pt-GCEs

Several research groups point out that RTIL improves a catalytic ability for ORR [20–24]. We have investigated ORR using a RTIL-modified Pt-GCE. The RTIL-modified Pt-GCE was prepared by rinsing Pt-GCE with dry acetonitrile, not 1.67 M KOH *iso*-propanolic solution. The surface state of the Pt-GCE was examined with infrared reflection absorption spectroscopy. As shown in Fig. 3(c), the Pt-GCE rinsed with dry acetonitrile indicated weak absorption related to the Me₃PrNTf₂N RTIL. We named it RTIL-modified Pt-GCE in this article.

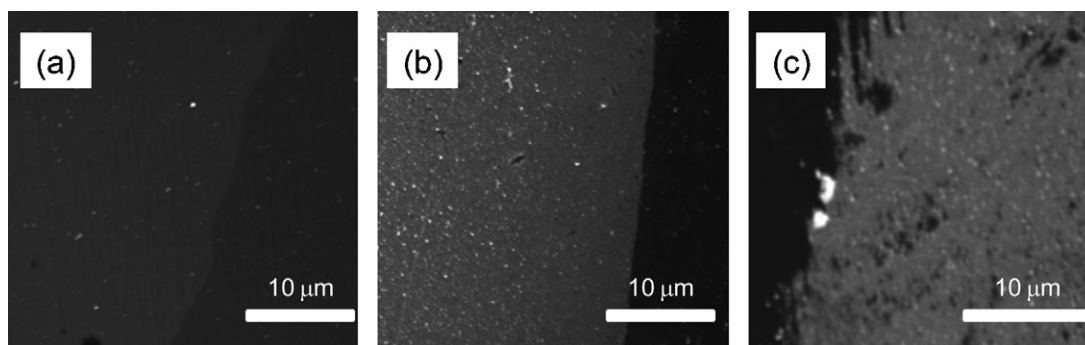


Fig. 6. SEM images of Pt-GCEs prepared at (a) 473 K, (b) 523 K, and (c) 573 K. The Pt-GCEs were rinsed with KOH *iso*-propanolic solution and nitric acid.

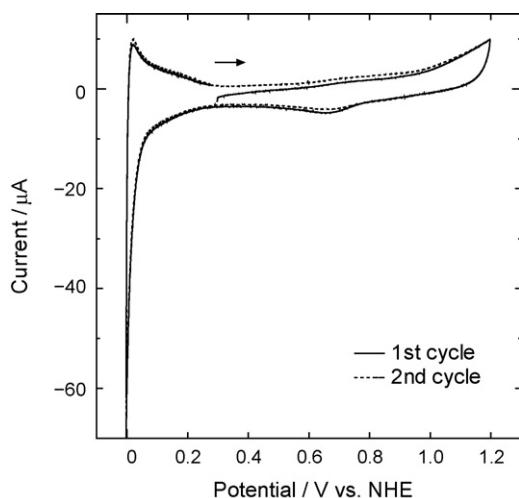


Fig. 7. Cyclic voltammograms recorded at a RTIL-modified Pt-GCE, on which CO monolayer was absorbed. The heat temperature for the Pt-GCE preparation was 573 K. The electrolyte was 0.5 M H_2SO_4 aqueous solution at 298 K. The scan rate was 10 mV s^{-1} .

The surface area of the RTIL-modified Pt-GCE was estimated by using CO stripping voltammetry, like original Pt-GCE described above. Fig. 7 indicates cyclic voltammograms recorded at the RTIL-modified Pt-GCE on which CO was absorbed. There is a no CO stripping wave, but is a reduction wave for hydrogen evolution. It implies that the RTIL-modified Pt-GCE is electrochemically active without CO poisoning. As expected, RTIL-modified Pt-GCE with CO poisoning reduced oxygen electrochemically (Fig. 8(a)). Voltammograms recorded at different initial potentials, e.g., +0.70 V, also showed a remarkably similar oxygen reduction wave. In fact, a number of groups report an effective interaction between RTIL and metal nanoparticles [28–31]. Probably the interaction prevents CO adsorption onto the Pt nanoparticles. Catalytic activity of the RTIL-modified Pt-GCE without CO poisoning toward ORR was investigated by cyclic voltammetry (Fig. 8(b)). This RTIL-modified electrode showed better catalytic ability than an original RTIL-modified Pt-GCE. The reason is not clear but the high activity would be due to the high oxygen solubility in the RTIL [3]. Using $\text{Me}_3\text{PrNTf}_2\text{N}$ RTIL as a solvent and a material, we succeeded to fabri-

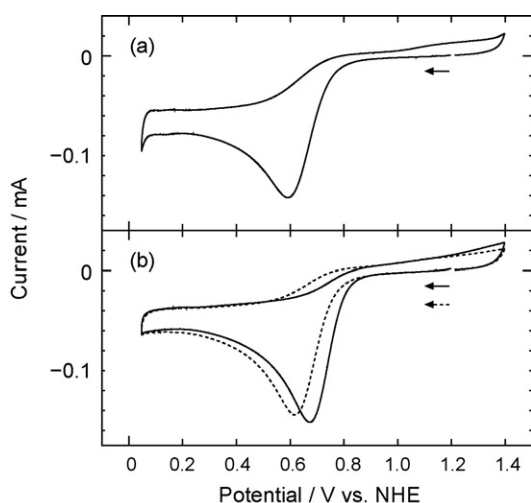


Fig. 8. Cyclic voltammograms recorded at (a) a RTIL-modified Pt-GCE with CO poisoning and (b) (—) a RTIL-modified Pt-GCE and (---) an original Pt-GCE in O_2 -saturated 0.5 M H_2SO_4 aqueous solution at 298 K. The heat temperature for the Pt-GCE preparation was 573 K. The scan rate was 10 mV s^{-1} .

cate a novel electrode, which has both O_2 reduction catalytic ability and anti-CO poisoning nature.

4. Conclusion

Pt nanoparticles can be produced by a Pt sputtering method onto $\text{Me}_3\text{PrNTf}_2\text{N}$ RTIL without any stabilizing agents. The Pt nanoparticles obtained by the Pt sputtering had mean particle size of ca. 2.3–2.4 nm independently of the sputtering time. The Pt-GCE prepared with the Pt-sputtered RTIL and a glassy carbon plate showed oxygen reduction activity but the activity varied with the preparation condition for the Pt-GCE. The $\text{Me}_3\text{PrNTf}_2\text{N}$ RTIL-modified Pt-GCE had better catalytic ability to ORR than the original Pt-GCE and never showed CO poisoning behavior.

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