

Applicability of a Channel Flow Double Electrode as a Quantitative Monitoring Method of Pt Dissolution under Potential Cycling

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Introduction

Sub-monolayer dissolution of Pt governs the electro-chemical surface area (ECA) loss of the cathode catalyst in a polymer electrolyte fuel cell (PEFC)^[1]. Potential cycling accelerates Pt dissolution, but the dissolution mechanism is unclear. The amount of the dissolution below 1.0V, where a PEFC’s cathode operates, is not yet quantified. At high potential range, 1.2~1.4V, Pt dissolution is caused by a place exchange between Pt and O^[2,3], but the valences of the dissolved Pt species (Pt²⁺ or Pt⁴⁺) are not yet identified. Clarification of the valences of the Pt species and their amount is necessary.

Experiments

A channel flow double electrode (CFDE) was applied to the study of sub-monolayer dissolution of Pt under potential cycling. In the CFDE, a platinum working electrode (WE) and a glassy carbon or gold collector electrode (CE) were placed at upstream and downstream, respectively, as shown in Fig.1. Pt ions dissolved at Pt-WE were collected at the CE electrode during potential cycling. The theoretical collection number N of the channel flow cell was 0.3, given the geometries of the WE and CE. Pt dissolution as Pt²⁺ was detected by setting the CE at 1.4 V vs. SHE where the dissolved Pt²⁺ is oxidized to Pt⁴⁺ on the CE. The dissolved Pt⁴⁺ was collected on the CE polarized at 0.7 V by reducing Pt⁴⁺ to Pt²⁺. Both Pt²⁺ and Pt⁴⁺ were detected on the CE at 0.3 V by reducing them to Pt(0). The amount of Pt²⁺ and Pt⁴⁺ dissolved in different potential regions within one cycle of CV was quantified using the collector current I_C. The amount of Pt²⁺, dissolved in the oxygen-reduction-reaction (ORR) region (0.4~1.0V), was calculated by the collector current I_C, and confirmed quantitatively by ex-situ inductively coupled plasma mass spectrometry (ICP-MS).

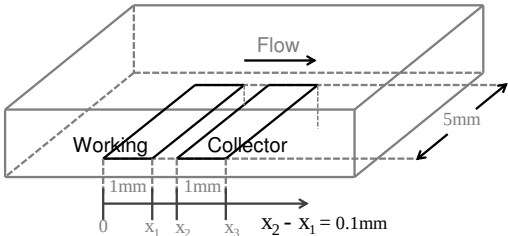


Fig.1 Schematic of a channel flow double electrode.

Results and discussion

Figure 2 shows the CV (I_W) of Pt between 0.4 to 1.0V and the collector current I_C obtained at the collector potential of 0.3V where both Pt²⁺ and Pt⁴⁺ are reduced to Pt. I_C starts to increase in negative direction when the WE is scanned from 0.6V to 0.8V, and is kept constant till 1.0V. The amount of Pt collected on the CE after 3000 cycles calculated by the collector current I_C was in good agreement with the amount of Pt deposit on the CE which was dissolved into aqua regia and then analyzed with ICP-MS (Table 1). The agreement between CFDE and ICP-MS confirms the reliability of the calculation by I_C.

Figure 3 shows the CV (0.4~1.4V) of Pt-WE and the CE current I_C obtained at two different collector potentials (E_C), 0.3 and 0.7V. At 0.3V, both Pt²⁺ and Pt⁴⁺, dissolved from the working electrode, are reduced to Pt on the collector electrode (Fig. 3 (left)). At 0.7 only Pt⁴⁺ is reduced but to Pt²⁺ (Fig. 3 (right)). The charge integrated using the CE current I_C from 1.2 to 1.4V (both anodic and cathodic scans) at 0.7V is 48% of that at 0.3V. Thus, the oxidation state of Pt above 1.2V is clarified as Pt⁴⁺. The amount of Pt²⁺ and Pt⁴⁺ dissolved in different potential regions within one cycle of CV is calculated by the collector current I_C and collection number N, and summarized in Table 2.

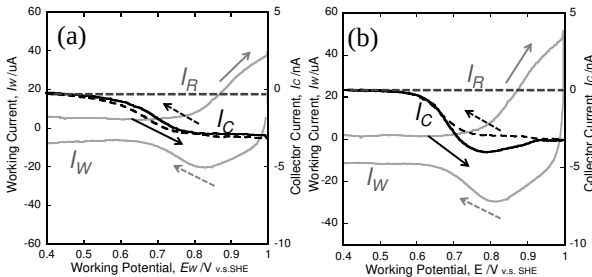


Fig.2 I_W-E_W and I_C-E curves in CV to 1.0V, using glassy carbon (a) and gold (b) collector electrode.

Table 1 Comparison of amount of collected Pt between CFDE and ICP-MS

E _C /V	Cycles	ΔW _{CFDE} /ng	ΔW _{ICP-MS} /ng
0.3	3,000	65.0ng (2.88ML)	52.5ng (2.33ML)
0.8	1,000	0	0

ML: monolayer

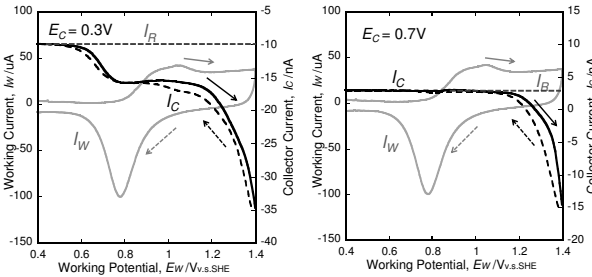


Fig. 3 I_W-E_W and I_C-E_W curves in CV to 1.4V at different collector potentials.

Table 2 Amount of dissolved Pt from per unit area ECA of the Pt working electrode at different potential regions in one cycle of CV from 0.05 to 1.4V at 20mV/s, calculated from collector current and collection number.

E _C /V	Anodic		Cathodic	
	0.6~1.2V	1.2~1.4V	1.4~1.2V	1.2~0.6V
0.3	0.25 (Pt ²⁺)	0.12 (Pt ⁴⁺)	0.14 (Pt ⁴⁺)	0.29 (Pt ²⁺)
0.7	No detection	0.09 (Pt ⁴⁺)	0.15 (Pt ⁴⁺)	No detection
1.4	I _R unstable	No detection	No detection	0.31 (Pt ²⁺)

I_R: residual current on CE

Reference

1. Y. Shao-Horn, W.C. Sheng, S. Chen, P.J. Ferreira, E.F. Holby, D. Morgan, Top. Catal., 46 (2007) 285.
2. Y. Sugawara, T. Okayasu, A. P. Yadav, A. Nishikata, T. Tsuru, J. Electrochem. Soc., 159 (11) (2012) F779.
3. H. Imai, K. Izumi, M. Matsumoto, Y. Kubo, K. Kato, and Y. Imai, J. Am. Chem. Soc., 131, 6293 (2009).