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著者(和文)	王 中奇
Author(English)	Zhongqi Wang
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The objective of this thesis was to understand the mechanism of Pt dissolution, which is important for the stability of Pt catalyst in polymer electrolyte fuel cells (PEFC). I constructed this thesis with six chapters, and each chapter was summarized as below.

In Chapter 1, I introduced the background and motivation of the thesis. I highlighted the merits that PEFC technology will bring to us, as well as the challenges for the massive production of FC vehicles and residential FC units for the next few decades. Pt dissolution is regarded as one of the critical issues that concerns the durability of PEFCs. From a scientific perspective, understanding the nature of this phenomenon is a necessary step for improving the lifetime of PEFCs.

In Chapter 2, I discussed the establishment of an in situ CFDE method for monitoring Pt dissolution under potential cycling. For simplicity, I used an electroplated Pt film as a bulk-like unsupported model electrode. The in situ CFDE analysis revealed that dissolution of Pt^{2+} may initiate near 0.8 V (vs. SHE) in an anodic scan. The amount of dissolved Pt^{2+} below 1.0 V was calculated using collector current (I_{CE}) and was confirmed by ex-situ inductively coupled plasma mass spectrometry (ICP-MS). The amount of Pt^{2+} and Pt^{4+} dissolved in different potential regions during potential cycling was quantified by I_{CE} for the first time. Comparison between CFDE data and ICP-MS data confirmed the reliability of the in situ CFDE method.

In Chapter 3, the in situ CFDE method was applied to the investigation of an impurity issue for PEFC: effect of chloride (Cl^-) on Pt dissolution. The experiments were conducted under both potentiostatic and potential cycling conditions. The CFDE system was modified to a channel flow multi electrode (CFME) system. To avoid the contamination of the entire CFME system by Cl^- , a liquid phase chloride ion gun is placed upstream of the double electrode. Under potentiostatic conditions, Cl^- enhanced Pt dissolution by forming PtCl_4^{2-} at potentials below 1.0 V and PtCl_6^{2-} above 1.2 V. Under potential cycling conditions, Cl^- accelerated Pt dissolution above 1.2 V by the enhanced formation of both PtCl_6^{2-} and PtCl_4^{2-} . The cathodic dissolution of Pt^{2+} during PtO_2 reduction was also increased in the presence of Cl^- .

In Chapter 4, I evaluated Pt dissolution from standard commercial PEFC catalyst, which is in the form of Pt nanoparticles supported on carbon (Pt/C). The in situ CFDE analysis focused on the detection of Pt^{2+} , which is the dominant Pt species produced during potential cycles below 1.4 V. On Pt/C, I observed both anodic and cathodic dissolution of Pt^{2+} under potential cycling; the later dominated at an upper potential limit (E_{U}) of 1.2 and 1.4 V. Both dissolutions were enhanced by elevating the temperature from 25 to 65 °C. In particular, the comparison between two Pt/Cs with a bulk Pt plate showed that Pt dissolution may depend on several parameters besides particle size. Moreover, I also evaluated Pt dissolution from Pt/C by ICP-MS. The results showed similarity with the CFDE data. In general, the CFDE showed its applicability to dissolution tests using supported nanoparticles. In the future, application of the in situ CFDE method for other Pt catalyst is also expected.

In Chapter 5, I sketch a model for dissolution of Pt under potential cycling in 0.5 M H_2SO_4 on atomic level. The model is distilled from the in situ CFDE analysis, and covers both anodic and cathodic Pt dissolutions from an electrochemical perspective. The anodic dissolution of Pt^{2+} goes through a single step from metallic to Pt^{2+} , and consumes unstable Pt atoms that present at edge sites. The place exchange process near 1.2 V triggers dissolution of Pt^{4+} . The cathodic dissolution is from reduction of PtO_2 at planar sites and produces Pt^{2+} . I hope the dissolution model may provide some strategic information for improve the durability of PEFCs.

In Chapter 6, I summarized the dissertation.