THE UNIVERSITY OF TOKYO

Office of University Professors
2-11-16 Yayoi, Bunkyo-ku, Tokyo, 113-8656, Japan

Yuriy Pihosh

TEL: +81-3-5841-7332
FAX: +81-3-5841-7039
E-mail: pihosh_y@arpchem.t.u-tokyo.ac.jp

Referee report on the doctoral thesis "Research and development of platinum-based cathode catalysts for proton exchange membrane fuel cells" by Mgr. Xianxian Xie.

The doctoral thesis presents a novel investigation into the development of Pt-based catalysts for the oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs). The research is driven by a desire to comprehensively explore the creation, analysis, and performance of advanced ORR catalysts produced using the magnetron co-sputtering technique, with the primary goal of improving the cost-effectiveness and longevity of PEMFC cathode catalysts. The author of this study made significant advancements through systematic examinations of the relationship between the composition, activity, and stability of bimetallic Pt-Au and ternary PtNi-Au alloy catalysts, as well as highly porous Pt-C catalysts created by electrochemical dealloying of a Pt-C-CeOx layer. The structure and chemical makeup of the catalysts were analyzed using various techniques, including scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The performance and stability of the fabricated cathodes were assessed through a range of electrochemical measurement systems, such as a rotating disc electrode system and SFC-ICP-MS, before ultimately undergoing testing in a real PEMFC test station.

Significant findings in this study include the determination of the optimal Pt to Au ratio in bimetallic Pt-Au catalysts, leading to enhanced stability while maintaining catalyst efficiency for the ORR, as discussed in Section 3.1. In Section 3.2, the author explored the potential for further improving the activity-to-stability ratio of ORR catalysts through Au doping of PtNi ternary alloys. Section 3.3 introduced the concept of selective dealloying of the Pt-C-CeOx ternary compound, prepared using magnetron sputtering, to create a highly porous Pt-C catalyst for ORR. These findings provide valuable insights for the development of efficient and durable ORR catalysts for fuel cell applications.

The author experimental work demonstrates a high level of quality, with some results already published in reputable journals. Based on the findings presented in this dissertation, I believe that Mgr. Xianxian Xie has met the necessary requirements for the doctoral degree. I recommend that the dissertation committee award Mgr. Xianxian Xie the title of Doctor of Philosophy (Ph.D.).

In relation to the thesis content, I have a few queries that may require clarification:

More important:

1) Experimental procedures need to be meticulously designed to ensure the accurate control of the thickness of the deposited co-catalyst film. While the author utilized AFM in Section 2.3.1 to measure the thickness of the deposited catalyst, there is a lack of detail in Section 2.2 regarding how the thickness of the deposited cocatalyst was controlled. It is crucial that the method employed to achieve this control be clearly outlined in Section 2.2 to facilitate verification. Furthermore, in Sections 3.1.1 to 3.1.2, it is imperative that the total thickness of Pt-Au alloys be explicitly stated to enhance clarity in the experimental process.
2) Section 3.1.3 on Page 45 examines the impact of Au on the catalytic activity of Pt-Au alloy-based catalysts. The results suggest that Pt maintains its catalytic activity when alloyed with 5% and 10% Au. However, a decrease in activity is observed when the Au concentration reaches 20%. Given that the Au concentration doubles from 10% to 20%, one may question the potential impact on catalytic activity if the Au concentration were to increase to 15%.
3) On page 56, the author discusses the significant stabilizing effect of Au within Pt-Au alloys, not only in idealized liquid-based half-cell experiments but also in PEMFC applications. I am curious if the author conducted durability tests on fabricated cathodes for PEMFCs.
4) In Section 3.2, the author discussed the results of incorporating ternary PtNi-Au alloy catalysts with varying compositions of Au in order to improve the activity and stability of ORR catalyst. The author observed that the activity of PtNiAu15 was slightly superior to that of monometallic Pt. It would have been informative if the author had also included the results of single cell performance tests using the ternary alloys in actual fuel cell devices. A comparison of the performance of proton exchange membrane fuel cells with Pt-Au and ternary PtNi-Au cathodes would provide valuable insights.
5) Section 3.3 on Page 79 discusses the leaching of CeOx from the Pt-C-CeOx catalyst layer during the electrochemical activation process. After 30 cyclic voltammetry scans, the morphology of Pt-C-CeOx undergoes significant changes, with almost all of the CeOx leaching out, resulting in the formation of a high surface area Pt-C catalyst, as evidenced by the SEM image in Figure 3.28a. The author did not specifically measure the surface area of the catalyst in this study. The rationale behind using CeOx in the fabrication of Pt-C-CeOx catalyst is not entirely clear, given that CeOx is not a stable material. It is possible that the presence of a small amount of CeOx in the electrode may enhance catalyst performance.

Minor comments:

1) Introduction. It is worth noting that aside from electrolysis, photocatalytic materials also have the capability to generate free carbon hydrogen. Unlike electrolysis, photocatalytic materials do not necessitate costly systems like the integration of solar cells with electrolysers to generate hydrogen.
2) Figure 2.1 illustrates the power supply and magnetron setup used in the experiments. It is important to specify whether a direct current (DC) or radio frequency (RF) magnetron was utilized to provide clarity and precision in the experimental setup.
3) Page 17. The author wrote `The conductive materials, like metals, can be sputtered using DC power supply`. There are various types of conductive materials that can be deposited using R.F. sputtering technique, such as titanium, aluminum, gold, silver, and others. On the other hand, DC sputtering process is typically utilized for magnetic materials and ceramics like nickel, iron, and carbon.

Tokyo, Apríl 2, 2024

Mgr. Yuriy Pihosh, Ph.D.