Reply to Comment on "Synthesis of Ordered Intermetallic $PtBi_2$ Nanoparticles for Methanol-Tolerant Catalyst in Oxygen Electroreduction"

With respect to the comments from Remona and Phani,[1] we apologize that we are not able to agree with them, on the basis of the following arguments:

Comment 1. "Xia et al.[1] have reported methanol tolerance and activity of $PtBi_2/C$ ordered intermetallic nanoparticles and their ORR (oxygen reduction reaction) activity. However, the authors present only very limited data and erroneous interpretation to prove its ORR activity. To evaluate the electrocatalytic activity of $PtBi_2/C$, the authors have compared its behavior with that of polycrystalline platinum. In this process, the authors have misinterpreted the curves in Figure 4. The peak marked 'oxygen reduction peak' (solid line) in the cathodic scan corresponds not to oxygen reduction reaction but to Pt-oxide reduction. Platinum hydrous oxides formed upon the surface oxidation during the anodic scan undergo reduction to form platinum crystallites. This is a very common phenomenon in electrochemical research literature, for example, ref 2. The discussion on page 5748, paragraph 2, is hence misleading."

Answer 1. We have worked in the area of electrocatalysis for more than 20 years and are very familiar with the surface electrochemistry of Pt. In particular, with more than 10 years of fuel cell catalysis, Pt catalyst electrochemistry and associated electrocatalytic ORR experience should be one of our core competencies. Our expertise and knowledge in these areas can be trusted.

Regarding the solid curve in Figure 4 for the Pt surface/ORR cyclic voltammogram (CV), at first glance, it looks like very much a surface Pt CV. However, if you take a closer look, you will find that it does contain the contribution from dissolved O_2. First, the CV baseline at zero current is not flat. It drifts off the baseline cathodically when the electrode potential is negatively scanned, indicating the contribution of an ORR current. Second, the area under the flat anodic wave in the potential range of 0.1−0.7 V usually for PtO formation is only around half of the area of the cathodic wave in the potential range of 0.3 to −0.2 V, suggesting that PtO reduction is not the only redox species contributing to this wave. Therefore, this cathodic wave is actually the sum of the contributions from both the PtO reduction and the O_2 reduction reactions. We believe that the readers who have Pt catalyst and ORR electrochemistry background should be familiar with this. This is why we did not give much detail in paragraph 2 on page 5748. Hopefully, the answer above addresses Remona and Phani's concern.

Comment 2. "There are problems with Figure 5 as well. In Figure 5, the $PtBi_2$ electrode is taken to high anodic potentials that favor dissolution of Bi. In our own experience and in accordance with the observations of Blasini et al.,[3] Bi leaches from the electrode surface indicating no significant increase in stability arising from the formation of an intermetallic phase with platinum. However, with the current sensitivity employed by the authors in their CV measurements, discerning such observations is difficult."

Answer 2. We did observe that when the electrode potential was scanned beyond 1.0 V, the dissolution of Bi occurred. However, when the potential was scanned below 0.6 V, the dissolution was not significant. This is why we only recorded the CVs in the potential range of $<$0.6 V (Figure 5).

Comment 3. "In addition, when the oxygen reduction current values are compared (Figure 4 and Figure 5b), the currents obtained for $PtBi_2/C$ are much lower than those for Pt/C. This means that $PtBi_2/C$ is not as active as Pt/C. Here, there is no noticeable change observed in the "faradic" part of the current in the cathodic scan on purging with oxygen or nitrogen (Figure 5a−c). There are ambiguities in the presented data."

Answer 3. First of all, one item that needs to be clarified is that in Figure 4 we used Pt rather than Pt/C.

In this paper, we had no intention to compare the catalytic activity of synthesized $PtBi_2/C$ with that of pure Pt, because the catalytic activity toward ORR is not the focus of this paper. We wanted to emphasize that (1) we have synthesized $PtBi_2/C$ catalyst and (2) $PtBi_2/C$ has ORR activity with superior methanol tolerance properties. With respect to the second point, $Pt/Bi_2/C$ has shown a methanol tolerance much superior to that of the Pt catalyst. The purpose of Figure 4 was to demonstrate that Pt has no methanol tolerance as it can catalyze not only the ORR but also the methanol oxidation reaction. However, in Figure 5, $PtBi_2/C$ has catalytic activity toward ORR but no catalytic activity toward the methanol oxidation reaction.

When comparing Figure 4 with Figure 5, the difference in units of both Y axes should be noticed (mA in Figure 4 and μA in Figure 5). With this in mind, the comment that "the currents obtained for $PtBi_2/C$ are much lower than those for Pt/C" is not valid.

The faradic part of the current in the cathodic scan changed significantly when the solution was switched from N_2 (Figure 5a) to oxygen (Figure 5b−c) purgings. We believe that the reader should have no problem in observing such a change if he/she reads this part carefully.

Comment 4. "In summary, the electrocatalytic reaction is misinterpreted and is not fully characterized in this paper, thus underestimating the weight of the electrocatalysis part in reporting this work."

Answer 4. We do believe that we may not have presented our work perfectly, but the interpretation of the electrocatalytic reactions in this paper has no fundamental problems. As scientists, we take a scientific attitude when we make a conclusion.

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