Reliable electrochemical measurement is the prerequisite for understanding and developing new electrocatalytic materials for energy conversion reactions. Thin-filmed rotating disk electrode (RDE) techniques are widely used for activity evaluation of electrocatalysts for a range of technologically important catalytic reactions such as oxygen reduction and oxygen evolution for application in fuel cells and electrolyzers. Generally, catalyst powders are made into homogenous catalyst ink and dropped onto a glassy carbon (GC) electrode to form a thin-filmed catalyst electrode, which was then mounted onto RDE for electrochemical measurement. There have been several works on the optimization of RDE testing protocols for oxygen reduction electrocatalysts. While most works highlighted the importance of a uniform catalyst thin film, a good electrode wettability with aqueous electrolytes is necessary for reliable activity evaluation of electrocatalysts. Due to the use of binders in the catalyst film and/or a hydrophobic surface of some catalyst powders, a good electrode-electrolyte wettability often remains a non-trivial task, leading to annoying visible or invisible bubbles at the electrode-electrolyte interface. These bubbles could have pronounced effect on the RDE activity measurement, which, however, are largely overlooked. A robust way to remove the bubbles and thus improve the wettability is highly desired yet still remains lacking.

In this report, we report a robust and easy-to-implement approach to improve the wettability and remove visible or invisible bubbles at the electrode-electrolyte interface for reliable and repeatable RDE measurement of electrocatalysts, using Ni-Fe oxide catalysts as a typical example (a widely-studied oxygen evolution reaction (OER) catalyst in recent years). This was achieved by triggering oxygen reduction at the catalyst-electrolyte-bubble triple phase boundaries at a constant reductive potential for a while, leading to oxygen depletion in the bubbles and thereby vanishing the bubbles. We also show that, insufficient wettability of catalyst electrodes due to visible or even invisible bubbles can lead to under-estimated activity for oxygen evolution reaction as well as inaccurate oxygen reduction reaction measurement. Once eliminating these bubbles at constant reductive potentials, the RDE tests can be repeatable and more reliable for activity assessment of electrocatalysts.

Experimental

Materials.—Two kinds of homemade Ni-Fe catalysts (NiFe-1, NiFe-2) were used in this work. The NiFe-1 oxide nanoparticles were prepared by using the organic phase reduction method as reported in the literature, which were then supported on Vulcan XC carbon black. Other carbon black supports such as acetylene black (AB), Ketjen black (KB), carbon nanotubes (CNT) and conductive carbon (Super P, SP) were also used to study the applicability of the method for improving electrode wettability. These catalysts were referred to as NiFe-1/AB, NiFe-1/KB, NiFe-1/CNT and NiFe-1/SP, respectively. For the synthesis of NiFe-2 catalyst, 2,6-Diaminopyridine, FeCl3 6H2O, NiCl2 6H2O and Ketjen black EC 600D were first homogeneously mixed and then dried to be used as the precursor. The as-prepared catalyst precursor was heated at 500 °C under Ar for 60 minutes and subsequently under NH3 for 10 minutes to obtain the final catalyst.

Electrochemical measurements.—The catalyst ink was prepared in isopropanol (IPA) solution (IPA:H2O = 1:1, v/v, using Millipore ultrapure water, 18 MΩ) with Nafion D-520 dispersion (5%, w/w) as a binder. Typically, 1.6 mg of catalyst powder was mixed with 1 mL IPA solution and 10 μL Nafion. The suspension was then ultrasonically dispersed for 10 minutes. A 10 μL portion of the ink was then dropped onto a 5 mm-in-diameter glassy carbon (GC) electrode and dried under a flow N2 atmosphere, leading to a uniform catalyst thin film with a catalyst loading of 0.08 mg/cm2. The filmed electrode was further dried in oven at 50 °C for 15 min.

All electrochemical tests were carried out in three-compartment electrochemical cell. The thin-filmed GC electrodes were mounted onto a RDE system (Pine Research Instrument, USA). A platinum wire and a Hg/HgO/Hg (1 M KOH) electrode were used as the counter and the reference electrode, respectively. Oxygen evolution activities were measured in O2-saturated 0.1 M KOH solutions with the RDE rotated at 1600 rpm. All potentials were referred to reversible hydrogen electrode (RHE), with 85% IR compensation.

Electron energy loss spectroscopy.—Electron energy loss spectroscopy (EELS) was conducted on a Tecnai G2 F30 field-emission transmission electron microscope (300 kV) equipped with Gatan Quantum 965ER dual EELS spectrometer, which allows to
Figure 1. OER measurement of the NiFe-1 catalyst with or without a prior constant reductive potential (CRP) treatment in O2-saturated 0.1 M KOH on RDE at 1600 rpm. (a) CV curves at 100 mV/s of OER tested directly on three independently prepared catalyst electrodes; the inset shows easily formed bubbles of different sizes when the electrodes were immersed into the electrolyte. (b) enlargement of the CV curve of test 1 in (a), showing the fluctuation of OER current. (c) CV curves of OER tested after a CRP treatment at 0.05 V for 20 s on two independently prepared catalyst electrodes; the inset photograph shows the absence of bubbles after CPR treatment. (d) Comparison of the LSV curves at 5 mV/s for OER tested directly when occasionally no visible bubble formed (see inset photograph), and for the subsequent OER tests on the same electrode after CRP treatment at 0.05 V and after additional 20 CVs between 0.05 and 1.0 V.

Results and Discussion

In order to study the effect of electrode wettability on their OER activity evaluation, we firstly prepared NiFe oxide nanoparticle catalyst (denoted as NiFe-1) supported on Vulcan XC carbon black (a widely used catalyst support) using a similar method as reported in the literature. Figure 1a presents the cyclic voltammetry (CV) curves of OER tested directly on the NiFe-1 catalyst from three separated tests following the same protocol. The inset photographs show that bubbles, despite of different sizes, can easily form on the electrode surface when the electrodes are immersed into the electrolyte, while occasionally one electrode with no visible bubbles was obtained. The corresponding three CV curves significantly differ from each other. The potentials at the current density of 10 mA/cm² (E₁₀) are 1.626 ± 0.006 V, 1.66 ± 0.01 V and above 1.7 V, respectively. It can be seen that with the increase of bubble size, the electrode-electrolyte interface area decreases, and the measured OER performance deteriorates accordingly. It can also be seen that, once the bubbles exist, the CV curves fluctuate significantly above 1.6 V (the OER region); the current density randomly changes instead of continuously increases or decreases (Figure 1b). The extent of fluctuation increases with the increase of bubble size. This fluctuation may be caused by the coupling between O₂ produced by OER and the bubbles, which could change the bubble shape/size, leading to varied OER currents.

We found that the bubbles formed due to the poor electrode wettability are difficult to be removed by simply high-speed rotating or repeated immersion/emersion of the electrodes. However, by applying a constant reductive potential (CRP, e.g., 0.05 V) for a short while (e.g., 20 s), bubbles can be effectively eliminated and the electrode wettability was significantly improved (as shown in the inset of Figure 1c). In two separate tests, the CV curves of OER obtained after holding at 0.05 V for 20 s substantially coincided with each other, where E₁₀ = 1.600 ± 0.005 V, and meanwhile the fluctuation of the E₁₀ after CRP treatment is reduced (5 mV only), thus greatly reducing RDE measurement error. More importantly, the measured OER activities are higher than those without a prior CRP treatment. We emphasize that, even without visible bubbles formed initially (Figure 1d), OER performance can be still improved after prior CRP treatment, indicating improved wettability by eliminating invisible micro-scale bubbles. After the CRP treatment, additional CVs between 1.0–1.65 V (Fig. 1c) or 0.05–1.0 V (Fig. 1d) did not result in further increased activity, indicating the absence of obvious surface cleanliness effect. The above results show that improving the wettability by prior CRP treatment can help to achieve repeatable and more reliable OER activity measurement.

Since the surface hydrophilicity of the support can have significantly influence on the catalyst electrode wettability, we further prepared a second NiFe catalyst supported on nitrogen-doped carbon black (NiFe-2). Although nitrogen doping has been reported to improve the hydrophilicity of carbon supports, we found that a prior CRP treatment under 0.05 V can still improve the wettability of the electrode and enhance the reliability of the OER test (Fig. 2a); after CRP treatment at 0.05 V for 20 s, the OER activity was again substantially improved. Accordingly, the double-layer capacitance in the CV curves under N₂ atmosphere (inset of Figure 2a) also increased, indicating increased electrochemical surface area.

In order to study the mechanism of eliminating bubbles and improving electrode wettability by prior CRP treatment, the chronocoulompermogram at 0.05 V on the NiFe-2 catalyst electrode with a visible simultaneously collect the zero-loss and core-loss spectra and thus eliminates any instrumental energy drift.
the electrode surface, an unexpected large reduction current density, around $5.7 \text{ mA/cm}^2$, was detected, even much larger than the theoretical limiting current density of $\text{OER}$ at 1600 rpm in $\text{O}_2$-saturated 0.1 M KOH solution (about $-5.5 \text{ mA/cm}^2$). In the stage (ii) (8–15 s), both the bubble size and current density decrease gradually. After 15 s (stage iii), the bubble vanished and a steady current density can significantly exceed the theoretical limiting current density. For the catalyst electrode without initially formed bubbles (Figure 2b, black line), the current density was large but then quickly decayed to $-5.7 \text{ mA/cm}^2$. We note that, the observed large reduction current on the electrode with bubbles in stage (i) can neither be ascribed to redox of NiFe oxide nor any non-faradaic capacitance current, which should increase with the decreasing bubble size, contrary with the experiment result.

The above results indicate that there is a direct correlation between the elimination of bubbles and $\text{ORR}$, which we explained in Figure 2c. Due to the oxygen-flowing environment during the OER measurement, the gas composition within the formed bubble is mainly $\text{O}_2$. In stage (i), as the $\text{O}_2$ gas concentration in the bubble is much higher (ca. 44 mmol/L) than the oxygen dissolved in the electrolyte (around 1.2 mmol/L),17 there is a dominant ORR process at the catalyst-electrolyte-bubble TPB, resembling a semi-immersion electrode. In this context, the ORR at the TPB is no longer limited by the diffusion of oxygen dissolved in the electrolyte and thereby the current density can significantly exceed the theoretical limiting current density. In stage (ii), as the $\text{O}_2$ in the bubbles depleting, the bubble size and the TPB area decreases, leading to decreased ORR current density. Finally (stage iii), when the $\text{O}_2$ was completely depleted, the bubbles vanished. At this time, the catalyst electrode transformed into a typical fully-immersed electrode and thus the ORR current density was limited by the mass transfer of dissolved oxygen. The reduction current density was thus reduced to $-5.7 \text{ mA/cm}^2$. Our results therefore also indicate that the existence of any visible or invisible bubbles due to poor electrode wettability not only change the electrode-electrolyte interface area but also perturb the limiting current density, thereby leading to inaccurate ORR activity assessment.

The CRP treatment can effectively eliminate visible bubbles in 20 seconds and also eliminate any invisible bubbles immediately (Figure 1d and Figure 2b, black line), thus improving the reliability of ORR measurement.

In Figure 3 we further studied how different potentials of CRP treatment impact the wettability of the NiFe-1 and the NiFe-2 catalyst electrode. These two catalysts present quite different ORR activities as shown in Figure 3a; the later performs much better ORR activity due to nitrogen-doping effect.18,19 For both catalyst electrodes, the apparent ORR activity increases with decreasing potential applied in the prior CRP treatment (Figures 3b, 3c), consistent with their increasing wettability (Figure 3d). However, the NiFe-1 catalyst requires CRP treatment at a lower potential (0.3 V or below) to get substantial improvement on the apparent ORR activity. By contrast, the NiFe-2 catalyst electrode can significantly increase the apparent ORR activity by CRP treatment at 0.5 V (Figure 3e). This is consistent with the elimination of visible bubble at 0.5 V on NiFe-2 catalyst, while a visible bubble still remained at 0.5 V on the NiFe-1 catalyst. (Figure 3d). The different behaviors of the two catalyst electrodes further validate our explanation in Figure 2c: the NiFe-2 catalyst is more ORR active, thus processes stronger capability to deplete oxygen, eliminate bubbles and improve the wettability. Nevertheless, for the NiFe-1 catalyst, it is still possible to improve the electrode wettability at 0.5 V with a longer CRP treatment time; in principle, any potential between 0 and 1.0 V could work as long as ORR can take place. This is particularly
Figure 3. (a) Comparison of ORR activity for the NiFe-1 and the NiFe-2 catalyst in O₂-saturated 0.1 M KOH at 1600 rpm, with background current densities corrected under N₂. (b, c) LSV voltammogram of OER tested after CRP treatment at different potentials for the NiFe-1 and the NiFe-2 catalyst, respectively. (d) Photos of the evolution of interface bubbles after CRP treatment at different potentials on the NiFe-1 and the NiFe-2 catalyst electrode.

important for those catalysts whose structures may be prone to change at lower potentials.

Figure 4 shows the EELS analysis of the valence change of Ni and Fe before and after OER test of the NiFe-2 catalyst. When the electrode shows poor wettability and visible bubbles, no energy shift of the Ni-L edge and Fe-L edge was found after the OER test without prior CRP treatment, demonstrating that most catalyst particles did not contact the electrolyte and thus remained unchanged. In contrast, the Ni/Fe-L edge shifts to higher energy loss after OER test with CRP treatment at 0.05 V, indicating a substantial oxidation of Ni and Fe during OER electrocatalysis on the electrode with improved wettability.

Figure 4. EELS of Ni-L edge (a) and Fe-L edge (b) in NiFe-2 catalysts before and after OER test with or without a prior CRP treatment at 0.05 V.

We further show that, electrode wettability improvement by CRP treatment not only applies to Vulcan XC carbon black support but also other types of carbon support such as acetylene black (AB, Figure 5a), ketjen black (KB, Figure 5b), and conductive carbon (Super P, Figure 5c) and carbon nanotubes (CNT, Figure 5d). Although the initial OER curve varies greatly for different supports due to randomly formed bubbles, all catalysts showed substantially improved OER performance after CRP treatment. Therefore, the prior CPR treatment for improving electrode wettability may be applied for a wide range of carbon-supported catalysts as well as other electrocatalytic materials. Slightly different OER performance after CRP treatment suggests an additional role of carbon supports in electrocatalytic activity.

Our results provide important insights into the RDE measurement of ORR and OER activities. For ORR measurement, since its potential range was already in the range of 0 – 1.0 V, the normally adopted CV or LSV techniques may already take the role of eliminating any visible or invisible bubbles. However, this need some time depending on the bubble size and the scan direction (seconds to several minutes), thus the initial CV/LSV result may not be reliable. The CV/LSV after a CRP treatment at 0.05 V is therefore always suggested. For OER measurement, it can be more problematic due to the potential range above 1.0 V. Our result can explain that why some previously-reported OER catalysts have to undergo a prior ORR measurement in order to achieve their optimum OER activities, a phenomenon that was previously uninterpretable yet can be fully understood from our work.²⁰

Conclusions

We developed a simple and robust method to eliminate interface bubbles and thus improve the wettability of thin-filmed catalyst electrodes immersed in aqueous electrolytes, providing a repeatable and reliable protocol for activity evaluation of electrocatalysts. Our re-
Figure 5. LSV curves of OER tested directly or tested after a prior CRP treatment at 0.05 V for 20 s for the NiFe-1 catalyst supported on different carbon supports. (a) acetylene black (NiFe-1/AB), (b) ketjen black EC 300JD (NiFe-1/KB), (c) super P (NiFe-1/SP), and (d) carbon nanotube (NiFe-1/CNT).

Results show that poor wettability of catalyst electrodes and the associated visible/invisible interface bubbles may result in an underestimated assessment of OER activity as well as inaccurate ORR activity evaluation, thus leading to failure RDE tests. We find that by applying a constant potential treatment at ORR reductive potentials (e.g., 0.05–1.0 V), the electrode wettability can be significantly improved, with visible/invisible bubbles being eliminated. This is because ORR was deliberately triggered at the electrolyte-catalyst-bubble TPB at the reductive potentials, thus depleting the O₂ gas in the bubbles and finally eliminating those bubbles. Our results provide an easy-to-implement way toward repeatable and more reliable RDE test for a wide range of technologically important electrocatalysts for energy conversion reactions.

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ORCID
Lin Gan https://orcid.org/0000-0003-3486-6016

References
1. U. A. Paulus, A. Wokaun, G. G. Scherer, T. J. Schmidt, V. Stamenkovic, V. Radmilovic, N. M. Markovic, and P. N. Ross, Journal of Physical Chemistry B, 106, 4181 (2002).
2. D. van der Vliet, D. S. Stremcik, C. Wang, V. R. Stamenkovic, N. M. Markovic, and M. T. M. Koper, Journal of Electroanalytical Chemistry, 647, 29 (2010).
3. M. Görlin, P. Chernev, J. Ferreira de Araújo, T. Reier, S. Dresp, B. Paul, R. Krahmer, H. Dau, and P. Strasser, Journal of the American Chemical Society, 138, 5603 (2016).
4. J. Suntivich, K. J. May, H. A. Gasteiger, J. B. Goodenough, and Y. Shao-Horn, Science, 334, 1383 (2011).
5. S. S. Kocha, K. Shinozaki, J. W. Zack, D. J. Myers, N. N. Karinuki, T. Nowicki, V. Stamenkovic, Y. Kang, D. Li, and D. Papageorgopoulos, Electrocatalysts, 8, 386 (2017).
6. K. Ke, K. Hiroshima, Y. Kamitaka, T. Hatanaka, and Y. Morimoto, Electrochimica Acta, 72, 120 (2012).
7. K. J. J. Mayrhofer, G. K. H. Wiberg, and M. Arenz, J. Electrochem. Soc., 155, P1 (2008).
8. M. Görlin, J. Ferreira de Araújo, H. Schmies, D. Bernsmeier, S. Dresp, M. Gleich, Z. Jusys, P. Chernev, R. Krahmer, H. Dau, and P. Strasser, Journal of the American Chemical Society, 139, 2070 (2017).
9. F. Domigi and P. Strasser, Advanced Energy Materials, 1600621 (2016).
10. D. Frießel, M. W. Louie, M. Bajdich, K. E. Sanwald, Y. Cai, A. M. Wise, M. J. Cheng, D. Sokaras, T.-C. Weng, R. Alonso-Mori, R. C. Davis, J. R. Bargar, J. K. Nørskov, A. Nilsson, and A. T. Bell, Journal of the American Chemical Society, 137, 1305 (2015).
11. L. Trotochaud, S. L. Young, J. K. Ranney, and S. W. Boettcher, Journal of the American Chemical Society, 136, 6744 (2014).
12. M. Gong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei, and H. Dai, Journal of the American Chemical Society, 135, 8452 (2013).
13. H. Zhu, S. Zhang, Y.-X. Huang, L. Wu, and S. Sun, Nano Letters, 13, 2947 (2013).
14. Y. Li, Y. Deng, Z. Pan, Y. Wei, S. Zhao, and L. Gan, Acta Phys. - Chim. Sin., 33, 2293 (2017).
15. K. P. Gong, F. Du, Z. H. Xia, M. Durstock, and L. M. Dai, Science, 332, 760 (2009).
16. M. Oezaslan, F. Hasche, and P. Strasser, Journal of the Electrochemical Society, 159, B394 (2012).
17. J. Zhang, Z. Zhao, Z. Xian, and L. Dai, Nature Nanotechnology, 10, 444 (2015).
18. K. Gong, F. Du, Z. Xian, M. Durstock, and L. Dai, Science, 323, 760 (2009).
19. M. Lefevre, E. Proietti, F. Jaqueen, and J. P. Dodelet, Science, 324, 71 (2009).
20. L. Du, L. Luo, Z. Feng, M. Engelhard, X. Xie, B. Han, J. Sun, J. Zhang, G. Yin, C. Wang, Y. Wang, and Y. Shao, Nano Energy, 39, 245 (2017).

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