Article type: Commentary

Impact of Surface Area in Evaluation of Catalyst Activity

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Electrocatalysis has been one of hottest research fields in recent years due to the global effort in exploring sustainable energy technologies. The central effort is to develop highly active electrocatalysts for those reactions playing key roles in fuel cells, electrolyzers, and rechargeable metal-air batteries, such as oxygen evolution, oxygen reduction, and hydrogen evolution reactions. A highly active electrocatalyst should be able to promote the reaction rate of the corresponding reaction. In kinetics, the activation energy should be lowered, and electrochemically a lowered overpotential should be observed at certain current density. Tafel plot is often used as a standard approach to present and compare the activities of catalysts, in which the applied potential or the overpotential at identical current density can be read. A low overpotential is usually the indicator of a good catalyst. For example, Figure S1 shows Tafel plots of oxygen evolution reaction (OER) on spinel $MnCo_2O_4$ oxides synthesized by several methods.[1] The dash line refers to the benchmark catalyst IrO_2.[2] In general, the plots (OER catalysts) located at the upper left region are less active than those located at the lower right region. Therefore, this figure basically shows that the activity of these spinel $MnCo_2O_4$ oxides are lower than IrO_2.

Tafel plots are generated based on the cyclic voltammetry (CV) curves, which is the method to record the response of the working electrodes (catalysts) in current (the charge transfer at the interface of electrode and electrolyte) to the applied potential. For a typical OER measurement, the recorded current includes the OER reaction associated charges as well as the capacitance contribution. After capacitance correction (and optional iR correction) [2], the “CV” curve at OER region (the reaction kinetic current versus the applied potential) then can be plot as a Tafel plot in a selected potential window. It is interesting to find that the Tafel plots among many papers are different in current density. Some papers use the current density normalized by the catalyst surface area, while some of them use the current density normalized by geometric surface area of working electrodes (disk surface area) in their Tafel plots. This actually generated some confusion within the community. Which one should be used or which one makes more sense?

Before answering the above question, one has to look at the difference between these two surface areas. If the catalyst being tested is a flat surface electrode, i.e. a single crystal surface electrode, the surface area of the catalyst can be treated same as that of geometric surface area of the electrode. [4] If the catalyst is in particles, especially in form of nanoparticles, usually they are drop-cast on a flat electrode, i.e. glassy carbon electrode (GCE) and then used as the working electrode. In this case, the roughness factor (the ratio of the catalyst surface area to the geometric surface area) can be very high and these two surface areas are significantly different. [5] Consequently, the Tafel plots can be significantly different.

To demonstrate this difference, we designed an experiment with a series of spinel Co_3O_4 powders with different particle size and investigated their OER performance using surface areas obtained by different approaches: 1) geometric surface area of GCE (disk surface area), 2) Co_3O_4 particle surface area by Brunauer–Emmett–Teller (BET) measurement, and 3) electrochemical surface area by non-Faradic double layer capacitance (carbon contribution excluded [6]).

The Co_3O_4 powders are synthesized by nitrate decomposition method, followed by annealing at different temperature (300~600 °C). Figure 1a shows the X-ray diffraction (XRD) patterns of as-synthesized Co_3O_4 powders. They all are pure in spinel phase. Figure 1b shows the OER CV curves. The inset is the close view on the redox region at 1.25 ~ 1.55 V vs RHE (versus reversible hydrogen electrode). The mass loading of Co_3O_4 on GCE is kept at 50 µg. These CV curves show that Co_3O_4 produced at lower annealing temperature gives higher redox peaks and OER currents. It seems that Co_3O_4 made at 300 °C gives the highest OER activity among these Co_3O_4 and with the increase of annealing temperature, the OER currents of these Co_3O_4 exhibit a gradual drop. Note that the annealing temperature difference actually caused the difference in particle size. This is evidenced in the particle size measured by BET approach. The Brunauer-Emmett-Teller (BET) specific surface areas of samples were measured with an ASAP Tristar II 3020 surface area and porosity analyzer. Nitrogen gas is used as the probe gas, which is a standard approach and allows to measure the surface areas as low as 0.01 $m^2\ g^{-1}$. The BET approach with nitrogen standard may be best suitable to particulate catalysts and it was used as early as 1977 to determine the surface area of a ruthenium dioxide catalyst by L. D. Burke, et. al.[7] As a result of particle size decrease, the specific surface area increased gradually from 4.78 to 23.98 $m^2\ g^{-1}$ according to BET measurements. Same trend is found in electrochemical surface area measured by non-Faradic double layer capacitance. The electrochemical surface area of these Co_3O_4 electrodes increased gradually from 2.07 to 8.33 cm^2 (from 4.14 to 16.66 $m^2\ g^{-1}$) along with the decrease of particle size.

Figure 2a shows the Tafel plots of OER on these Co_3O_4 using the current density normalized by geometric surface area of GCE. It clearly shows the size dependent OER activity, i.e. Co_3O_4 with small particle size gives higher OER activity and vice versa, like the size effect reported elsewhere.[8] However, the Tafel plots using the current density normalized by BET and electrochemical surface areas do not show such remarkable size dependence (Figure 2b and 2c). In fact, the size dependence observed in Tafel plots by geometric surface area of GCE should be the consequence of the particle surface area variation, which is caused by the particle size difference. Figure 2d shows the positive correlation between BET surface area, OER currents by geometric surface area of GCE, and the charge associated with the reduction of Co^{4+} to Co^{3+} at the potential range of 1.25 ~ 1.55 V vs RHE. Such positive correlations strongly indicate that the increased OER activity (by GCE geometric area) should be ascribed to the smaller size of Co_3O_4 particles, which gives higher surface area of catalyst and more surface Co. However, according to what has been observed in oxygen reduction reaction (ORR) on Pt [5], the size effect refers to the influence of particle size on the intrinsic activity (the activity normalized by the catalyst surface area, instead of electrode geometric area, which is usually used to exclude the influence of mass loading variation on electrodes). Here, the Tafel plots in Figure 2b and 2c should represent the intrinsic activity of these Co_3O_4 since the catalyst surface area is used (each represents one approach to obtain catalyst surface area). It is reasonable to say that there is no size dependent OER among these Co_3O_4. This is probably true for oxide catalysts according to the reported OER mechanism, where the molecular orbital theory of a single metal cation is employed.[3] That says little influence of the particle size of oxide catalysts to surface cations' electronic structure. Some exception should be noticed, such as particle size induced spin state change of active cations on particle surface.[9]

Figure 3 shows the Tafel plots of OER on Co_3O_4 made at 300 °C, in which the OER currents are normalized by the three surface areas as mentioned above. It can be seen that the three Tafel plots are parallelly aligned with the same Tafel slop and the only difference is the current density value. This is not surprising since only the current density is affected by using different surface area values. However, surprisingly the plot using geometric surface area of GCE is located at the right side of the figure with a distance of ~0.084 mA cm^2 from the other two plots using BET surface area and electrochemical surface area. Such a location difference, based on the principle of Tafel plot, tells the activity difference. However, the three plots are by the same material. This difference can be also seen in the Tafel plots of Co_3O_4 made at 400, 500, and 600 °C (not shown). All of them tell that the plots using geometric surface area of GCE will give a high OER activity. As mentioned above, the activity normalized by the geometric surface area of electrodes cannot represent the intrinsic activity of a material. It can only tell the activity of the tested electrode from an engineering aspect (more practically meaningful in developing devices). In Figure 3, the Tafel plots of benchmark IrO_2 extracted from the literature [2] is also added for comparison purpose. It can be seen that the activity of Co_3O_4 can be much higher than IrO_2 if its activity is normalized by GCE geometric area. However, this does not truly reflect the intrinsic activity of these materials. If normalized by oxide particle surface area, a reasonable comparison can be given, i.e. the activity of Co_3O_4 is lower than IrO_2.

In summary, we have briefly discussed the influence of surface areas on the Tafel plots using the example of Co_3O_4 particles. We can see that using geometric surface area of electrodes can "boost" the OER activity to a very high value in Tafel plots. Such “boosted” activity is an artificial effect and does not reflect the intrinsic activity of a catalyst material. However, it reflects more the activity of the tested electrode and practically meaningful to water electrolysis devices. This reminds us that the overpotential at 10 mA cm^{-2} (where disk area is used) should not be used as an activity evaluation standard for OER catalysts, which however now is very popular in literatures. To compare the performance of two catalysts, the activity normalized by catalyst surface area (intrinsic activity) is recommended. Besides BET and non-Faradic capacitance measurements, there are a few other methods, such as under-potential deposition, for measuring the surface area of electrocatalysts electrochemically.[10] However, to get catalyst surface area may be challenging to some novel materials (developing novel materials to catalyze OER actually is a major effort in the field currently), where BET method is not applicable and electrochemical surface area is not measurable. More effort may be necessary in exploring alternative approaches to measure the surface area of “novel” catalysts.

Acknowledgement

Z. Xu acknowledge the funding support from the Singapore Ministry of Education Tier 2 Grants (MOE2017-T2-1-009) and the Singapore National Research Foundation under its Campus for Research Excellence and Technological Enterprise (CREATE) programme. Z. Xu also thanks The 1st International Symposium on Electrocatalysis and Electrosynthesis, held in Changsha, China, from March 30 to April 1, 2018, in which the issues of activity evaluation in literatures was raised up by beloved colleagues and students.

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Figure Captions:

Figure 1. (a) XRD patterns of Co_3O_4 synthesized at different temperature. (b) CV curves of these Co_3O_4 at the potential range of 0.9-1.6 V (vs RHE). The inset shows a close view in the potential range of 1.25-1.55 V (vs RHE), in which the redox of Co^{3+}/Co^{4+} can be seen.

Figure 2. (a) Tafel plots of OER activities normalized by geometric surface area of electrodes (disk surface area) (a), BET surface area of Co_3O_4 catalysts (b), and electrochemical surface area obtained by non-Faradic double layer capacitance (c). (d) The positive correlation between BET surface area, OER currents by geometric surface area of GCE, and the charge associated with the reduction of Co^{4+} to Co^{3+} at the potential range of 1.25 ~ 1.55 V vs RHE.

Figure 3. Tafel plots of OER on Co_3O_4 made at 300 °C, in which the OER currents are normalized by the three surface areas as mentioned above. The Tafel plots of benchmark IrO_2 extracted from the literature [2] is also added for comparison purpose. If the geometric surface area of electrodes (disk surface area) is used for current density, the OER activity can be “boosted” superior to IrO_2 easily.