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An *Operando*-Raman study on oxygen evolution of manganese oxides: Roles of phase composition and amorphization

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ABSTRACT

Manganese oxide catalysts exist in various forms of polymorphs, which have direct influence on their oxygen evolution reaction (OER) performance. However, their structure flexibility under working conditions remains a great challenge for identifying their active structures. In this work, OER performances of manganese oxide electrocatalysts with representative phase compositions (birnessite, bixbyite) were examined using *operando*-Raman spectroscopy. The results indicate that catalysts containing birnessite composition do not exhibit apparent OER activity before an charging activation process. Shifting of Raman peaks around $\sim$640 cm^{-1} can serve as an indicator for predicting their OER onset potentials. The amorphization of mixed-phase catalyst is in favor of this activation and reduces the OER onset potential by 120 mV. Moreover, the coexistence of bixbyite-like Mn(III) center and amorphized birnessite composition combines their abilities of catalyzing both electrochemical and chemical steps, creating a more bias-efficient reaction channel. This leads to the lowest Tafel slope and improved activity in the high overpotential region, suggesting that amorphous OER catalysts with structural flexibility can facilitate the OER kinetics.

1. Introduction

Oxygen evolution reaction (OER) is an essential part of the water splitting process [1–4]. Among the vast candidates of OER electrocatalysts, manganese-based OER catalysts receive increasing attention due to its resemblance to the oxygen evolution cluster in natural photosystem II [5–11]. Many catalysts of this series have been synthesized in various phases and compositions with excellent activity. Correspondingly, there have been many publications devoted to the investigation of the performance dominating factors [12–19], however this issue is still far from being well elucidated. Birnessite (δ-MnO_2), hausmannite (Mn_3O_4), groutite (α-MnOOH) and bixbyite (α-Mn_2O_3) phases have all been claimed to be active for water oxidation reaction [20–22]. In the birnessite category, there have been many publications concerning the different OER activity between triclinic and hexagonal types [18,23,24]. Nevertheless, Manganese atoms can exist with various oxidation numbers between +2 and even +5 [16]. This property bestows strong structure flexibility upon manganese oxides and easy phase transformations, especially for those synthesized at room temperature with low crystallinity [16,25]. Such prepared electrocatalysts are likely to undergo transitions around OER potential, catalyzing the OER reaction in a different structure from its "rest" state. This also results in frequent phase coexistence and amorphization, adding difficulty to the identification of active structures [14,16,26,27].

Due to its ability to combine real-time spectroscopic characteristics with activity data retrieved at working conditions, *operando* technique plays an indispensable role in the field of catalysis study [28,29]. Thanks to its simple, robust design and sensitivity towards materials with low periodicity, Raman spectroscopy is an effective technique for the study of materials with low crystallinity during electrochemical reactions [30,31]. It has been applied in the mechanistic study of supercapacitive behavior of manganese oxides [25,32,33] and in the transformation of Ni-Fe OER electrocatalyst under anodic potential [34,35]. However, due to the convolution of multiple electrochemical reactions in the catalyst bulk or on the surface, investigation of OER mechanism of manganese oxide catalysts under working condition remains a complicated task.

In this work, the effect of phase compositions and amorphization on OER performance of three typical manganese-oxide-based electrocatalysts [20,36] were investigated using *operando*-Raman

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spectroscopy. To build a structure-activity relation, Tafel plots were exploited to extract the OER onset potential and information about the rate-determining steps. The structure flexibility, activation process and OER onset potential under working condition are well correlated. These results confirmed the influence of birnessite and bixbyite compositions on OER pathways, and suggest that structure flexibility originating from amorphized environment facilitates the formation of active centers.

2. Experimental

2.1. Instruments

Raman spectra were collected using 532 nm diode-pumped solid-state laser (Changchun New Industries Optoelectronics Technology Co., Ltd.) and a commercial Raman spectrometer (Invia, Renishaw plc.). A water-immersion objective with a numerical aperture of 1.2 was utilized for improved signal collection efficiency (LUMPLFLN-60XW, Olympus Corp.). Laser power at sample surface was kept around 0.2 mW to minmize sample damage (for more details see Section 3 of supporting information). Typical spectrum collection time was 3 min. 3–4 spectra were collected under each bias to ensure result homogeneity. The samples were loaded into a custom-built *operando* cell. A potentialstat worked to perform electrochemical experiments (VersaSTAT 3, Princeton Applied Research). Platinum was used as counter electrode (99.99%, Lijiu Co.). An Ag/AgCl reference electrode was used (Leici Co.).

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcat.2018.08.007.

2.2. Sample preparation and OER current measurement

All external biases are converted to biases relative to reversible hydrogen electrode (RHE) unless mentioned otherwise. All electrocatalyst samples are prepared according to the previous report. The areas of these electrodes were kept at 1 cm^2.

The Bir/Bix sample [36] was prepared by performing 25 cycles of cyclovotammetry between + 1.95 V and -0.95 V against Ag/AgCl (Leici Co.) reference electrode (not converted to RHE considering the high resistivity of the dilute deposition solution, as stated by the reporter) in 50 mL of 0.05 mM $Mn(OAc)_2$ (Sinopharm Chemical Reagent Co., Ltd) solution on an ITO working electrode. Preparation of Bir sample [36] was conducted by constant potential deposition at 1.35 V vs. Ag/AgCl reference electrode in 50 mL of 5 mM $Mn(OAc)_2$ (Sinopharm Chemical Reagent Co., Ltd) solution for 15 min on an ITO working electrode. The Bix sample was prepared [20] by constant current deposition (0.25 mA/cm^2) in 50 mL solution with 0.25 M $MnSO_4$ and 0.25 M Na_2SO_4 (Sinopharm Chemical Reagent Co., Ltd) for 25 min on an ITO working electrode, followed by calcination at 773 K for 60 min. (For the synthesis of model compounds used in the identification of Raman spectra see supporting information.)

0.1 M KOH solution was used to perform *operando*-Raman experiments. Linear sweeping voltammetry (LSV) was performed between 0.95 V and 1.8 V vs. RHE at a rate of 20 mV/sec. A full CV cycle with the same range and rate was scanned before LSV to stabilize the electrodes. Tafel slopes were scanned from 1.2 V to 1.85 V at a rate of 0.5 mV/sec.

3. Results and discussion

3.1. General characterizations: electrochemical, XRD and SEM/AFM

A series of samples, including a birnessite MnO_2 sample (referred to as Bir) and a bixbyite α-Mn_2O_3 sample (referred to as Bix), and a less-ordered electrocatalyst with mixed phase compositions (referred to as Bir/Bix) were synthesized according to methods reported in literatures [20,36]. The linear sweeping voltammetry (LSV) plots of these electrocatalysts are shown in Fig. 1. It can be found that Bir has the lowest OER activity among these samples, with OER current well below 0.1 mA in the tested potential region. Bix has the lowest OER onset potential, starting to show detectable OER current at around 1.4 V. The Bir/Bix sample exhibits OER activity at a slightly higher potential than Bix (around 1.5 V), however it exhibits the sharpest current increasing trend. It eventually overtakes the activity of Bix at 1.83 V and higher potential, possessing the highest activity in the high overpotential region.

The electrochemical behaviors and OER mechanism of these catalysts were further analyzed using Tafel plot (shown in Fig. 2a). For hydrogen evolution (HER) and OER reactions in which water is the reactant, Tafel plot provides the ability of extracting important parameters reflecting electrochemical reaction mechanism while minimizing many disturbing effects, such as electrochemically active surface area, amount of loading and electrical conductivity (See Fig. S1 for more discussion). These Tafel curves are composed of three segments for each: a vertical or slowly-increasing pre-OER segment in the low overpotential region, followed by an exponentially increasing Tafel segment. In the high overpotential region an upward-bending resistivity segment is observed. Each of these segments corresponds to a specific current dominating factor [37]. To interpret these plots, an equivalent circuit is presented in Fig. 2b, which contains solution resistance (R_s), double layer capacity (C_{dl}), electrochemical pseudocapacitance (C_{ec}) and charge transfer resistance (R_{ct}) [38].

In the pre-OER segment, OER process does not take place due to insufficient external bias. This is frequently observed in many transitional-metal-based OER electrocatalysts, since the active centers, which are crucial in catalysing OER, often requires an appropriate bias to form [34,39]. On the other hand, birnessite has been long known as electrochemical pseudocapaictors [24,25,32]. For Bir and Bir/Bix samples with birnessite composition, the vertical behavior in this region indicates that the overall Tafel curve is dominated by charging of the electrochemical pseudocapacitance C_{ec}, due to its similarity to the *i-E* characteristics of capacitors (current almost irrelevant against applied bias) [40]. To give a more precise description of the potential required to initiate the OER, the pre-OER and Tafel segments are extrapolated, and the intersection is defined as the characteristic OER onset potential. Bir/Bix shows decreased onset potential (1.48 V, all potentials here and in the following text are with respect to RHE) compared to Bir (1.62 V), although still higher than that of Bix (1.35 V), in

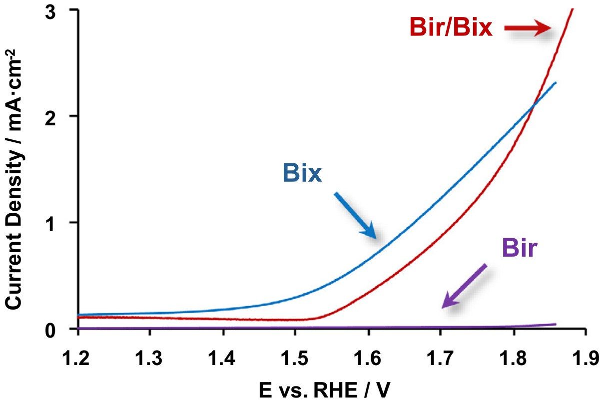

Fig. 1. LSV curve of Bir (purple), Bix (Blue) and Bir/Bix (Red) electrocatalysts in the oxygen evolution region.