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Rationalizing the Influence of the Mn(IV)/Mn(III) Red-Ox Transition on the Electrocatalytic Activity of Manganese Oxides in the Oxygen Reduction Reaction

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ABSTRACT

Knowledge on the mechanisms of oxygen reduction reaction (ORR) and descriptors linking the catalytic activity to the structural and electronic properties of transition metal oxides enable rational design of more efficient catalysts. In this work ORR electrocatalysis was studied on a set of single and complex Mn (III) oxides with a rotating disc electrode method and cyclic voltammetry. We discovered an exponential increase of the specific electrocatalytic activity with the potential of the surface Mn(IV)/Mn(III) red-ox couple, suggesting the latter as a new descriptor for the ORR electrocatalysis. The observed dependence is rationalized using a simple mean-field kinetic model considering availability of the Mn(III) centers and adsorbate-adsorbate interactions. We demonstrate an unprecedented activity of Mn_2O_3, ca. 40 times exceeding that of MnOOH and correlate the catalytic activity of Mn oxides to their crystal structure.

1. Introduction

Transition metal oxides (TMOs) have attracted much attention as promising catalysts for the electrochemical oxygen reduction reaction (ORR) in alkaline media in view of their potential applications for metal-air batteries, fuel cells, and, recently, also for regenerative fuel cells [1–3]. Manganese oxides are of particular interest as low cost, abundant and green materials with high electrocatalytic activities in the ORR and the OER (oxygen evolution reaction) [4]. It is the observation, early in the 19th century, of the sensitivity of MnO_2 cathode of the Leclanché's element to air, which stimulated interest in oxygen electrocatalysis on Mn oxides and lead to the introduction of zinc-air batteries (see Ref. [5] and references therein). Since then, numerous studies have been performed in order to evaluate the activity, understand the ORR mechanism, and unveil structure - activity relationships in ORR electrocatalysis on Mn oxides [6–14]. Despite the fact that numerous single and complex Mn oxides have been studied as the ORR catalysts, the main structural and compositional factors determining their electrocatalytic activity are still poorly understood, and the values of electrocatalytic activities reported in the literature are often contradictory. This may be attributed to a number of factors, such as electrochemical degradation of Mn oxides at excessively high or low electrode potentials [11], or insufficient electronic conductivities of some Mn oxides, prompting researchers to add carbon to the catalytic layers [6,14–17]. Considering that in alkaline media carbon also participates in the ORR [18], singling out the contributions of the oxide and of carbon to the ORR activity is not a trivial task, and the reported activities may change by order(s) of magnitude depending on the presence of carbon and on its amount [17]. A yet another difficulty relates to the fact that there is no common view on which parameter to use to characterize the catalytic performance. For the case of the OER, this is well discussed by Fabbri et al. [19]. Materials are compared in terms of the ORR onset (or potential at a specified current)

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neglecting the catalyst loading and its specific surface area, or in terms of current at a defined potential (usually 0.9 V vs RHE) normalized to the mass or surface area of the oxide. These uncertainties complicate understanding of the structure-activity relationships in the ORR electrocatalysis by oxides.

Already early studies attempted to find ORR/OER descriptors which could be further used for guiding the design and optimization of the TMO catalysts. A prediction of the OER activity increase with the M-OH bond strength for metal electrodes [20], raised attempts to correlate the OER activity of perovskite oxides with the enthalpy of formation of corresponding hydroxides [21]. Importance of the red-ox transitions of metal cations has also been recognized [22], supported by a "volcano" relationship of the OER activity *vs*. the enthalpy of lower-to-higher oxide transition for a wide range of oxides [23]. Goodenough and Cushing [24] and Suntivich et al. [25] applied molecular orbital considerations and proposed the e_g-orbital occupancy activity descriptor, which postulates that the latter determines the strength of the oxygen bonding to metal oxide surfaces and thus the ORR/OER activity. By studying a range of perovskite-type oxides of various transition metals it was conjectured that an e_g occupancy slightly below 1 is required for achieving high ORR activity [25,26].

In the last decades application of first-principles computational methods using density functional theory (DFT) offered a molecular level insight into the elementary steps of reactions on surfaces. Su et al. [27] performed periodic DFT calculation for Mn oxides, and considered an "associative" mechanism of the ORR and OER occurring through the formation of OH_{ads}, O_{ads} and OOH_{ads} intermediates. By establishing a "scaling relationship" between the adsorption strength of OOH_{ad} and that of OH_{ad}, Su et al. suggested Gibbs energy of OH formation (ΔG_{OH}) as a unique ORR descriptor and predicted similar ORR activities for Mn_3O_4, Mn_2O_3 and MnO_2.

Recently, from combined experimental and kinetical modeling studies of the ORR on perovskite-type oxides, we discovered that the measured ORR activity strongly depends on the amount of carbon which had to be introduced in the catalytic layer for improving its electronic conductivity and maximizing the utilization of the catalyst active centres, and worked out the tools to extract the specific activity of oxides [17]. Then, we came to the conclusion that Mn-perovskites are much better ORR catalysts compared to Co-based counterparts, the latter only acting as co-catalysts in tandem with carbon. Finally, by studying the ORR and the oxidation/reduction reactions of its stable intermediate, hydrogen peroxide, and by combining experimental studies with a mean-field kinetic model, we arrived at the conclusion that the apparent $4e^-$ ORR on (Mn and Co) TMOs with the perovskite structure follows a "series" $2e^-+2e^-$ pathway, where the O_2 molecule is first reduced to hydrogen peroxide, the latter reacting on the catalyst surface to produce water [28,29]. We put forward a kinetic model, which is based on the reaction mechanism shown in Fig. 1. The model is not only capable of reproducing the experimental data on the ORR and H_2O_2 red-ox transformations in a wide range of experimental parameters, but helps predicting factors responsible for the activity of TMOs. The mechanism shown in Fig. 1 builds on earlier studies [7,24–26,28] and is based on the assumption of the key role played by the M(n)/M(n + 1) red-ox transition (steps 1 and 5 in Fig. 1). Note that red-ox transformations of Mn cations in the potential interval of the ORR/OER have been confirmed by *in situ* XAS [10,30] and *ex situ* XRD studies [31].

Armed with the knowledge acquired recently on the oxygen electrocatalysis on TMOs, in this publication we seek for establishing the structure-activity relationship by studying a set of Mn oxides adopting different crystal structures (Fig. 2): Mn_2O_3, MnOOH, $A_{1-x}A'_xMnO_3$ perovskites ($LaMnO_3$, $PrMnO_3$, $La_{0.8}Ca_{0.2}MnO_3$), MnO_2, and Mn_3O_4. All of them (with the exception of MnO_2) primarily contain Mn(III) cations (Mn_3O_4 contains 2/3 Mn (III) and 1/3 Mn(II), and $La_{0.8}Ca_{0.2}MnO_3$ contains 4/5 Mn(III) and 1/5 Mn(IV)), and are expected to satisfy the e_g-occupancy requirement of efficient ORR electrocatalysis proposed in refs [24,25]. By juxtaposing the ORR activity measured with a rotating disc electrode (RDE) with surface red-ox properties of oxide materials studied with cyclic voltammetry (CV), we arrive at the conclusion that the potential of the surface Mn(IV)/Mn(III) red-ox transition can be used as a descriptor of the ORR activity. We complement this with the mean-field modeling in order to rationalize the observed behavior and to provide a self-consistent phenomenological description of the interfacial red-ox mediator ORR catalysis. We explore adsorbate coverage effects and a likely influence of lateral adsorbate interactions.

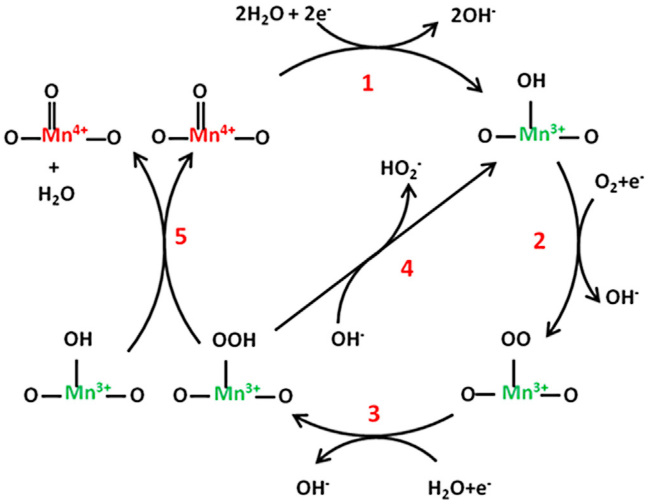

Fig. 1. Proposed oxygen reduction mechanism. Step 1 is O_{ad}/OH_{ad} conversion accompanied by Mn(IV)/Mn(III) red-ox transition (Mn(IV) = O/Mn(III)-OH). Step 2 is electrochemical O_2 adsorption, which proceeds via displacement of adsorbed OH species accompanied by an electron transfer, and can only occur on Mn(III) sites (green). Step 3 is coupled electron and proton (from water molecule) transfer. Step 4 is adsorption/ desorption of hydrogen peroxide, the latter dissociating into HO_2^- in alkaline medium. Step 5 is a chemical step resulting in formation of two Mn(IV) sites (red). For further details see text and Electronic Supplementary Information (ESI). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Experimental

2.1. Sample preparation

MnOOH sample was prepared according to the procedure described in Ref. [32]. Aqueous solution of $KMnO_4$ was added to a stirred solution, containing sucrose, $MnSO_4$ and HNO_3. The resultant mixture was refluxed at 100 °C under constant stirring for 4 h. MnO_2 and Mn_3O_4 were prepared by thermal decomposition of MnOOH for 2 h at 240 °C (in air) and 600 °C (in Ar), respectively (*cf.* thermal gravimetric analysis in Figure S1 of ESI). Three Mn_2O_3 samples were studied in this work. The first one (**Mn_2O_3_wet1**, refer to Table 1 for sample notations) was prepared by aerosol spray pyrolysis [33]. The aerosol was produced from 0.3 M $Mn(CH_3COO)_2$ aqueous solution using ultrasonic generator operated at 2.64 MHz. The obtained aerosol was directed to the furnace by an air flow where pyrolysis occurred at 800-900 °C. The second sample (**Mn_2O_3_wet3**) was obtained by calcination of an amorphous product of