



Determining the elementary steps of surface reactions by isotope exchange[☆]



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ARTICLE INFO

Article history:

Received 21 January 2014

Received in revised form 14 July 2015

Accepted 23 July 2015

Available online 11 September 2015

Editor: J. Maier

Keywords:

Isotope exchange

Elementary steps

Oxide catalysts

Oxygen vacancy

Pulse isotope exchange technique

ABSTRACT

A novel method, using isotope exchange is discussed for determining the elementary steps in surface reactions. The method is presented using oxygen exchange with oxides as a working example. We apply the method to a series of possible exchange reactions and show how to differentiate between them. The slow step and possible fast reversible steps preceding the slow one can be identified. We pay attention to the role of oxygen vacancies in the dissociation of oxygen molecules on oxides. The experimental requirements are that the amount of ¹⁶O/¹⁸O molecules desorbed from the oxide is monitored with time while two parameters are changed: the oxygen partial pressure in the experiment and the concentration of acceptors in the oxide. The most suitable experimental method to provide the necessary data is the pulse-response ¹⁶O/¹⁸O isotope exchange (PIE) technique.

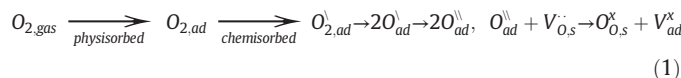
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1. Introduction

There is a considerable difficulty in determining the elementary steps in surface reactions. It is even more difficult to determine the whole series of consecutive steps in a reaction. We first demonstrate the difficulty with existing methods when trying to answer the question of the role of oxygen vacancies in the dissociation of oxygen molecules on oxides. We shall then show how processes of oxygen adsorption can be analyzed for their elementary steps from experimental data obtained by using a suitable isotope exchange procedure.

There is increasing evidence suggesting that oxygen vacancies on oxide surfaces are involved in the dissociation step of adsorbed oxygen molecules. This dissociation is of interest in heterogeneous catalysis of oxidation reactions as well as in electrocatalysis at the cathode of solid oxide fuel cells (SOFCs) or of metal–oxygen battery.

The interaction of an O₂ molecule with an oxide is usually assumed to include dissociation on the surface, followed by incorporation of individual oxygen ions into vacancies in the oxide. An example is,



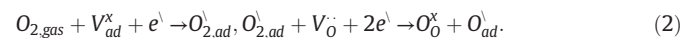
[☆] Principles of this work were presented during the 4th Polish Forum Smart Energy Conversion and Storage, Krynica, Poland 1–4.10.2013.

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where we have used the Kröger–Vink notation for point defects [1], “ad” denotes an adsorption site on the oxide surface and V_{O_s}[·] denotes an oxygen vacancy in the outer most atomic layer “s” of the bulk of the oxide. An example is presented schematically in Fig. 1. The molecule dissociates on the surface before meeting an oxygen vacancy. Different oxygen species were reported to be present. For example, on LSM (La_{0.8}Sr_{0.2}MnO_{3-x}) two species were identified as O_{2,ad}^{\cdot} and O_{2,ad}^{\cdot\cdot} (at 600 °C) [2]. It is, however, difficult to determine experimentally which of the elementary steps take place in the interaction between an O₂ molecule and an oxide.

One can envision cathodic reactions in SOFCs, in which the dissociation of the oxygen molecules takes place with the involvement of one or even two oxygen vacancies in the oxide surface. Fig. 2a shows, schematically, a process in which one oxygen vacancy dissociates an oxygen molecule by absorbing an oxygen ion into the vacancy. The O₂ molecule from the gas phase is either adsorbed onto the surface and dissociates when it interacts with an oxygen vacancy, V_O (Fig. 2a) or it directly enters a vacancy (Fig. 2b). As a result of the O₂–V_O interaction one oxygen ion is incorporated into the oxide leaving another oxygen atom/ion on the surface.

Computer simulations by Matrikov et al. [3] suggest the two versions of the process presented by Eqs. (2) and (3) below. In one, the O₂ molecule is first chemisorbed on the surface to form a superoxide, O_{2,ad}^{\cdot\cdot}. The later radical then interacts with an oxygen vacancy to form a lattice oxygen leaving the second ion, O_{ad}^{\cdot\cdot}, chemisorbed on the surface. The following reaction is an example,



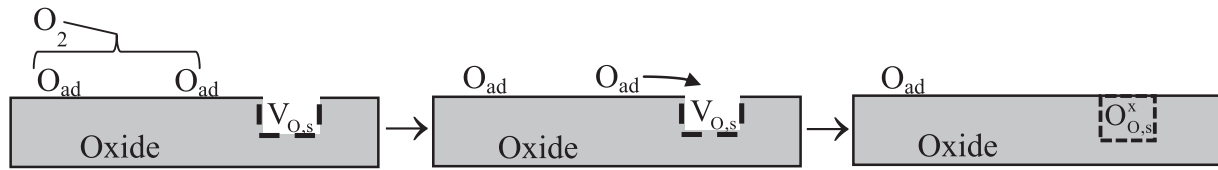
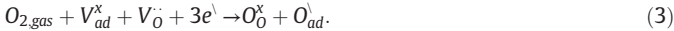


Fig. 1. Schematics of the dissociation of an oxygen molecule O_2 on the surface of an oxide followed by the incorporation of one of the dissociated oxygen ions into a vacancy. The lattice is presented as a continuum and the oxygen vacancy as an indentation. The charge of the particles is not given (except in $O_{O,s}^x$) as different processes are possible.

In the second process the oxygen molecule directly reacts with a vacancy which leads to dissociation, resulting again in one lattice oxygen ion and one chemisorbed oxygen ion. The following reaction is an example,



Other theoretical calculations also suggest that in the reduction process of an oxygen molecule on an oxide the molecule may dissociate by interaction with an oxygen vacancy (Fig. 2) [4,5]. However, those calculations do not rule out dissociation of the adsorbed molecules on the oxide surface and only then an interaction of the single, adsorbed oxygen atom/ion with an oxygen vacancy (Fig. 1).

One can envision the interaction of two oxygen vacancies simultaneously with the two atoms of an oxygen molecule. This process is presented, schematically, in Fig. 3. The following reaction is an example,



It is anticipated that this process can take place mainly when the distance between the vacancies is close to the distance between the two oxygen atoms in the molecule. Further discussion of this case is outside the scope of this paper.

A few experimental methods try to cope with the question of the specific role of oxygen vacancies in cathodic reactions. Cathodic reactions in solid oxide fuel cells, oxide oxidation and heterogeneous catalysis on oxide catalysts may have many steps in common. Thus, experiments examining the latter two processes provide relevant information for the cathodic reaction, as well. Merkle et al. [6] have devised a set of experiments to determine the steps involved in the oxidation/reduction of Fe–SrTiO₃. The oxide under test is exposed to an atmosphere, the oxygen partial pressure, $P(O_2)$, of which is abruptly changed. The oxidation reaction rate after a sudden $P(O_2)$ change is measured and combined with measurements of the electron-hole generation in the oxide under UV illumination. With these experiments and the analysis developed, assuming a single rate determining step, the authors are able to reduce the large number of possible reaction steps consistent

with Eq. (1) to a few alternatives only. Yet, they are unable to provide an answer to the question, is the absorption of an oxygen ion in an oxygen vacancy a necessary condition for the dissociation of an O_2 molecule.

Yoo and Bouwmeester [7] applied the pulse-response ^{18}O – ^{16}O isotope exchange method (PIE) to SrTi_{1-x}Fe_xO_{3-δ} and were also unable to determine unambiguously if a vacancy is involved in the dissociation of the oxygen molecule.

In another approach one tries to change the oxygen vacancy concentration by cathodic polarization. It is experimentally observed that applying cathodic polarization to an oxide electrode in an SOFC, enhances the rate of oxygen reduction. There are different explanations for that enhancement. Y. Jiang et al. [8] examine cathodic polarization of LSM (La_{0.8}Sr_{0.2}MnO_{3-δ}) on YSZ (Y₂O₃ stabilized ZrO₂) and attribute the electrode reaction rate enhancement to an increase in the oxygen vacancy concentration in LSM under cathodic polarization. The later conclusion is supported by L. Wang et al. [9] who examined, under cathodic polarization, electrodes made of LSM as well as of LSCF (La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-δ}) and BSCF (Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-δ}). The later authors, however, conclude that the rate of diffusion of the oxygen vacancies in the surface layer is also of importance. Reduction enhances both the vacancy and electron concentrations. It is, hence, an increase in the ambipolar diffusion coefficient, which enhances the electrode reaction rate. However, W. Wang et al. [10] come to a different conclusion. They claim that the enhancement of the oxygen reduction reaction, at the LSM electrode, under cathodic polarization, is due to removal of SrO segregated on the electrode, the SrO having an inhibiting effect on the reaction. Only under excessive cathodic polarization does the role of oxygen vacancies become significant. Backhaus-Ricoult et al. [11] provide, yet, a very different explanation. They claim that under polarization Mn migrates from the LSM electrode onto the YSZ solid electrolyte (SE) turning the surface of YSZ into a mixed-ionic–electronic-conductor (MIEC), thereby significantly widening the triple phase boundary (TPB) which is the active area of the cathode. Baumann et al. [12] show that cathodic polarization of an LSCF (La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ}) electrode (on YSZ) enhances the oxygen reduction rate and that this enhancement is associated with changes in the chemical composition of

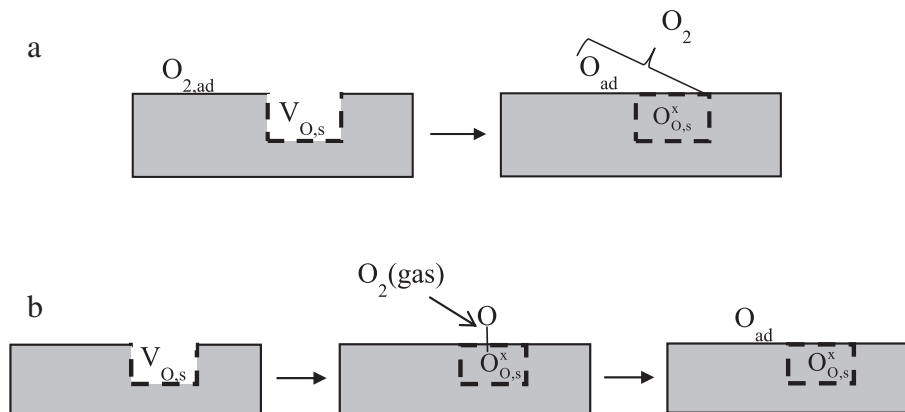


Fig. 2. 2a: A vacancy is used for the dissociation of O_2 after the molecule is adsorbed on the oxide surface. Charges are not indicated (except in $O_{O,s}^x$). 2b: A vacancy is used for the dissociation of O_2 . The molecule coming from the gas phase enters directly into the vacancy. Charges are not indicated (except in $O_{O,s}^x$).

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