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Oxygen electroreduction on Ag(1 1 1): The pH effect

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Abstract

The rotating ring disk method (RRDE) is applied to investigate the pH effect on oxygen reduction reaction (ORR) on Ag(1 1 1) single crystal surface in 0.1 M KOH and 0.1 M $HClO_4$. In 0.1 M KOH, the ORR proceeds through $4e^-$ reaction pathway with a very small (0.5–2.5%) peroxide formation in the entire potential range. In 0.1 M $HClO_4$ the onset potential for the ORR is shifted for ca. 400 mV toward the higher overpotentials compared to the 0.1 M KOH solution. At the low overpotentials, in 0.1 M $HClO_4$ the ORR proceeds entirely as a $2e^-$ process, i.e, 100% H_2O_2 formation. At higher overpotentials, the initial mixed a $2e^-$ and $4e^-$ reduction is followed by the potential region where the ORR proceeds entirely as a $4e^-$ process, with H_2O formation as a final product. The pH dependent shift in the onset of the ORR as well as the reaction pathway has been explained based on both: a thermodynamic analysis of pH independent rate determining step, and on the pH dependent change in availability of surface active sites and adsorption energies of molecular oxygen and reaction intermediates.

Keywords: Rotating ring disk method; Oxygen reduction reaction; Reversible hydrogen electrode; Ag(1 1 1); pH effect

1. Introduction

In response to increasing awareness of environmental factors and limiting energy sources, modern surface science must solve challenging problems in the area of clean energy conversion, such as fuel cells. Two of the fundamental catalytic limitations that have plunged the development of fuel cells for more than a century still remain: it is difficult to use any fuel different than pure hydrogen and a high overpotential for the oxygen reduction reaction even on the most catalytically active materials such as Pt. In spite of many attempts in the last decade by researchers and fuel cell developers to create non-Pt catalyst for low temperature (<200 °C) air cathodes, Pt remains the catalyst of choice at least for acid-based fuel cells.

The situation in alkaline electrolyte is rather different from acid electrolyte. Alkaline electrolytes present many opportunities for non-Pt catalysts for the ORR. Materials that have little or no measurable activity for the ORR in acid have substantial, even commercially practical, levels of activity in alkaline solution. The first technological alkaline fuel cell, developed by the group of Bacon at the University of Cambridge in 1950s, utilized non-Pt electrodes, a Ni anode and a lithiated NiO cathode (electrolyte was 30 wt.% aqueous KOH). Today, in the space shuttle's alkaline fuel cell, rapid oxygen reduction is achieved using high surface area gold crystallites, where metallurgical densification and loss of surface area of the gold electrocatalysts is overcome by alloying the gold with the platinum. The platinum is located in the core of the binary alloy electrocatalyst particle and therefore is not directly involved in oxygen electroreduction.

Although the remarkable pH effect has been known for some time, the fundamental reason is still elusive. In this paper we analyze the effect of pH on the oxygen electroreduction on Ag(1 1 1) surface, by comparing the ORR activity in 0.1 M KOH and 0.1 M $HClO_4$ solutions (resulting in the pH difference of approximately 12 units). To explain this effect we use combination of a thermodynamic rationale based on the energetics of the $O_2/O_2{}^-$ (superoxide radical anion) redox couple, and the kinetic analysis involving the influence of adsorbed anions from the supporting electrolyte not directly involved in the oxygen electroreduction reaction (so-called spectator species).

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2. Experimental

The Ag(1 1 1) single crystal (0.283 cm^2) was chemically polished before each experiment in a mixture of CrO_3 and HCl according to the procedure based on the work of Hamelin et al. [1], originally developed from a patent quoted in Ref. [2]. Here we'll give just a brief overview. Prior to the polishing, the crystal was kept for ca. 15 min in concentrated H_2SO_4. After rinsing with triply pyrolitically distilled water, the crystal was dipped several times into concentrated $HClO_4$ (only the crystal face that was to be polished was exposed to the acid solution). The crystal was then transferred into the CrO_3–HCl mixture. During this procedure, a white-yellow precipitate is formed on the crystal, which makes the solution cloudy (again, only the surface which was to be polished was exposed to the solution). After rinsing the crystal in triply pyrolitically distilled water, the crystal was immersed into a concentrated ammonia solution for several minutes (ca. 5–10 min). After the rinsing with water, before mounting in the RRDE configuration, the crystal was kept once more for 10–20 min in concentrated H_2SO_4 and rinsed with water. After mounting in the RRDE setup, the electrodes were transferred into a thermostated standard three compartment electrochemical cell and immersed into the Ar-purged electrolyte at ≈293 K (Ar: Bay Gas Research Purity; 0.1 M KOH: Aldrich Semiconductor Grade, 0.1 M $HClO_4$: Aldrich, double distilled, prepared with triply pyrodistilled water) under potentiostatic control at ≈−0.2 V. The reference electrode was a saturated calomel electrode (SCE) separated by a closed electrolyte bridge from the working electrode compartment in order to avoid contamination. All potentials, however, refer to that of the reversible hydrogen electrode (RHE) in the same electrolyte. The collection efficiency of the RRDE setup was $N = 0.22 \pm 5\%$.

3. Results

3.1. Cyclic voltammetry

In alkaline solution adsorption/desorption processes on Ag(1 1 1) are highly reversible, as reveled from a cyclic voltamogram (CV) in Fig. 1. The CV is in a very good agreement with previously published data [3–7] and can be used as criterion for cleanliness and quality of the prepared surface. In particular, after relatively flat current–potential profile at most negative potentials, which corresponds to the charging/discharging of the "double layer", a broad reversible OH adsorption peaks are followed by the third potential region where additional OH^- adsorption serves as a precursor for a bulk oxide formation, i.e. above 1.18 V (corresponding to 0.342 V on the standard hydrogen electrode scale).

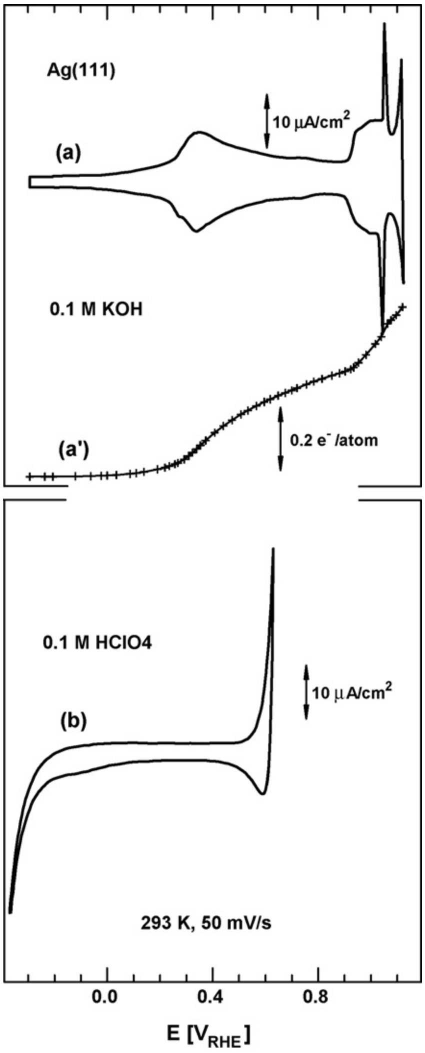

Fig. 1. (a) Cyclic voltammetry curve in argon-purged 0.1 M KOH (room temperature and sweep rate 50 mV/s); (a′) fractional charge per atom, obtained by integrating the anodic sweep direction of cyclic voltammetry (from (a)) after accounting for the surface atom density of Ag(1 1 1) orientation ($\sigma = 1.38 \times 10^{15}$ atOMS/cm^2); (b) cyclic voltammetry curve in argon-purged 0.1 M $HClO_4$ solution (room temperature and sweep rate 50 mV/s).

After subtracting the charge required for the charging of the double layer, the total charge density transferred through the interface Q (μC/cm^2) was obtained by integrating the i versus E curve in the anodic and cathodic sweep directions. Notice that there is a perfect charge balance between the OH_{ad} layer formation in anodic sweep direction and the reduction of OH_{ad} in the cathodic sweep direction. This is somewhat different from the irreversible adsorption of oxide on Pt single crystal surfaces [8], suggesting that Ag(1 1 1)–OH_{ad} and Ag(1 1 1)–O_{ad} interactions are weaker relative to the Pt–O interaction. Based on the total charge transferred through metal/electrolyte interface a fractional surface charge per atom was assessed and displayed in Fig. 1(a′). The fractional surface charge per Ag(1 1 1) atom is in direct correlation with the OH_{ad} surface coverage, which shows a characteristic S-shape behavior. In particular, a slow initial rise of θ_{OH} is followed by a steep increase in OH_{ad} surface coverage, subsequently followed by a plateau where saturated surface coverage by reversibly adsorbed OH_{ad} is reached, corresponding to ca. 0.35 e^-/atoms The even steeper increase in $\theta_{OH_{ad}}$ on more positive potentials (≥1.18 V) corresponds to the irreversible-bulk oxide formation. This region is of no interest here, since ORR occurs entirely in the potential range <1.18 V.

All the pronounced features in the cyclic voltammetry characteristic for 0.1 M KOH solution become much less