Adsorption and absorption of hydrogen species on silver electrode in alkaline solution

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The processes of adsorption and absorption of H atoms on silver electrode in alkaline media has been studied using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The potential range in the CV studies has been between -0.1 and -1.6 V /Ag-AgCl. In the first cycle, two cathodic and three anodic peaks have been observed. The H atom electroabsorption current peak at ca. -0.6 V /Ag-AgCl, which appears at second cycle, is assigned to hydrogen absorption states. Nyquist plots consist of two overlapping semi-circles of variable diameters depending on the extent of the cathodic dc-potential offset. Hydrogen absorption occurs simultaneously with the hydrogen evolution reaction and competes with it. The H atoms are converted to H₂ rather than being sorbed into the polycrystalline Ag when the potential is more negative. These H atoms in the bulk of Ag electrode can be removed only by heating the electrode on flame.

The hydrogen evolution reaction (HER) is one of the most important reactions in electrochemistry. Oxidation and reduction of hydrogen on the electrode surface have important applications in the development of fuel cells. The hydrogen evolution reaction on silver has been investigated, from various aspects, using methods such as steady-state polarization, cyclic voltammetry and in situ Raman spectroscopy. Different mechanisms are suggested for hydrogen reaction on silver in alkaline solution.

We have recently reported the electrochemical adsorption, and diffusion of hydrogen into the polycrystalline platinum electrodes in both acidic and alkaline media. Adsorption and diffusion of hydrogen into polycrystalline Ni have also been studied in this laboratory. In this study we have used the method of cyclic voltammetry to evaluate the nature of hydrogen oxidation and reduction at silver polycrystalline electrode in alkaline solutions.

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Experimental

A polycrystalline Ag with surface area of 0.5 cm² was used as working electrode. A platinum mesh and Ag/AgCl (saturated KCl) were used as counter and reference electrode, respectively. All potentials are with reference to the Ag/AgCl electrode. Before each experiment, the working electrode was heated on a flame followed by chemical etching in solutions of NH₄OH and NaCN+H₂O₂ to remove silver oxide. The electrolyte solution was 0.1 M NaOH prepared from analytical grade (p. a. Merck) and doubly distilled water. Cyclic voltammograms were recorded using potentiostat/galvanostat (EG&G 273A, USA) controlled by M270 software, via a GPIB interface.

Results and discussion

The cyclic voltammograms of the active silver electrode in 0.1M NaOH electrolyte in the potential range of ~ -0.1 and ~ -1.6 V are presented in Fig. 1. In the first cathodic sweep they are characterized by a number of cathodic (C₂, C₃) and anodic (A₁, A₂, A₃) peaks. In the second cathodic sweep, a new peak emerged at ~ -0.6 V (C₄). According to Fig. 1, upon further potential sweeps, the current intensity of C₂ was increased until 2.2 mA, while the height of C₃ decreased.

In order to find out how the final potentials influence the oxidation peaks, the initial potential was fixed at ~ -0.1 V and different final potentials were applied. The results are demonstrated in Fig. 1b (zoomed at around A₁ and A₂ peaks). As it is observed the height of the A₁ and A₂ peak increases until ~ -2 V. At more negative potentials, these peak heights were decreased.

Changing cathodic potential to more negative values in an anodic sweep results in the increase in current intensity of all peaks upon increasing the cathodic potential at a constant anodic potential limit (Eₐ = ~ -0.1 V).

It is already reported that, these peaks in the range of ~ -0.1 to ~ -0.4 V are the results of the oxidation and adsorption of OH⁻ on silver (OH₃ads) electrode. According to the results with shifting the potential to more negative value, the height of anodic peak must increase. It is noted that the adsorption of OH species decreases when the potential is shifted to more
negative values. So these peaks are the result of reaction that occurs in the more negative potentials and are not related to adsorption of \( \text{OH}^- \).

According to the results obtained from Fig. 1, it is suggested, atomic hydrogen that appears in the first cycle maybe absorbed into the substrate (\( \text{H}^{\text{abs}} \)). The \( \text{H} \) species on the surface and just within can be electronically different, depending on the extent of partial electron transfer associated with adsorption and absorption of \( \text{H} \). Not only the absorbed \( \text{H} \) atoms can diffuse into the electrode material, but also these \( \text{H}^{\text{abs}} \) may also oxidize (\( \text{A}_1 \)). Some of them remain at the same site, so they will not contribute into the solution (\( \text{H}^{\text{eq}} \)). Therefore we could conclude that in the second cycle, \( \text{C}_1 \) peak is the result of reduction of \( \text{H}^{\text{eq}} \) in the bulk of Ag electrode. The appearance of \( \text{A}_1 \) and \( \text{C}_1 \) peaks are closely related to the start of formation of atomic hydrogen on the electrode surface. As hydrogen adsorption is dependent on the (negative) potential, shifting the potential to more negative values until -2 V (Fig. 1b), will increase the height of the oxidation peaks, which are related to the \( \text{H}^{\text{abs}} \). It is important to recognize that any further increase in potential would result in most of the discharged \( \text{H} \) being converted to \( \text{H}_2 \) rather than being absorbed into the metal. So, in more negative potentials the height of oxidation peaks (\( \text{A}_1 \), \( \text{A}_2 \)) decrease.

The result of reduction and adsorption of hydrogen on silver electrode is presented in Fig. 1. Intensities of \( \text{C}_2 \) and \( \text{C}_3 \) peaks in successive cycles can be explained by assuming that \( \text{H} \) atom electrosorption reactions on polycrystalline silver display a multiplicity of current peaks, which are associated with different \( \text{H} \) atom states on the metal. The relative contribution of these peaks changes according to the topography of the electrode. The arrangement of the superficial atoms exhibits a great variety of shapes. Further, the way in which the atoms are arranged to build up an adsorption site determines the electronic properties and therefore the electrosorptive characteristics of the site. So, in further cycling, \( \text{H} \) atoms can diffuse from one site to another site on the Ag surface. Similar process on Pt surface has been reported previously.

It was observed that the results shown in Fig. 1, were reproducible when the electrode was heated. This phenomena is an evidence for diffusion and absorption of hydrogen in the bulk of Ag electrode. By heating the electrode, \( \text{H}^{\text{abs}} \) is removed from the
crystalline structure of Ag, and therefore the electrode after heating shows the same behavior as observed in
Fig. 1, (an active electrode with no reaction)\textsuperscript{12,13}. These results are in good agreement with the
mechanism reported by Gao at al.\textsuperscript{18} for absorption of H in the hydrogen evolution reaction on different
substrates.

The results of electrochemical impedance measurements at different potentials on Ag electrode show two overlapped capacitive loops at $E < -1.5$ V. (Fig. 2a). At higher catholic potentials the capacitive
loops seem to be practically separated. Figure 2b presents the measurement at $-1.7$ V where H$_2$ bubbles
were clearly seen over the electrode surface. The centers of the semicircles in the Nyquist plots are
depressed below the $Z_{(Im)}= 0$; such a behavior is
characteristic of an electrode, the impedance of which is commonly represented by constant phase element
(CPE) in the equivalent circuit.

The corresponding equivalent circuit is shown in
Fig. 2. Real and imaginary components, obtained at each dc-potential were analyzed using the complex
nonlinear least squares (CNLS) programs developed by Boukamp to estimate the value of the equivalent
circuit elements\textsuperscript{19}. The CPE$_1$ is usually associated with porosity of the working electrode\textsuperscript{20}. The Nyquist
plots for Ag surface consist of a higher frequency
process, which is assigned to electron transfer
relaxing the double layer capacitance ($R_d$, CPE$_1$) and
a lower frequency component (CPE$_2$, $R_2$) associated
with the modulation of the hydrogen coverage, with
potential shifting. At low potentials, both dispersion
processes are resolved. At higher potentials the
second dispersion process decreases indicating that
now the coverage of hydrogen is reaching a constant value\textsuperscript{20}.

The values of CPE$_2$ were strongly potential
dependent. It is concluded that the large CPE$_2$ value at
$-1.5$ V in a parallel connection with resistance $R_2$,
together with a small value of the CPE$_2$ exponent $\varphi_2$, may actually arise because of significant sorption of H
into the surface of Ag electrode.

According to Nyquist plots and cyclic voltammograms the rate of hydrogen desorption step becomes higher than that of the parallel step (hydrogen absorption reaction) when potential is set
more negatively.

Based on the above discussion, it can be concluded
that (i) H sorption takes place as a parallel reaction to
the desorption steps in hydrogen evolution reaction.
When the electrode potential is low ($< -2$ V) the
contribution of hydrogen absorption becomes more
important. Increasing potential ($> -2$ V) leads to high
H$_2$ evolution. (ii) The appearance of peak at $-0.6$ V
after the first cycle is related to H sorption into the
bulk of electrode. The sorbed H-species in sequential
cyclic voltammetry experiments will not leave the
surface. Heating the electrode on flame is the only
way to remove this sorbed H-species. And (iii) the
contribution of hydrogen absorption and subsequent
diffusion $H_{abs}$ becomes more important as the
electrode potential is low. When potential is set more
negatively, the reaction proceeds according to the
H$_2$O discharge and desorption of the adsorbed
hydrogen from the surface.
References