Comparative, enhanced, induced adsorption phenomena on polycrystalline gold electrode

Theses (PhD)

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Introduction, aims

Our country has a long tradition of the radiotracer study of solid/liquid interfacial effects. As a result of the improvement of the radiotracer method important research centres have developed countrywide at the Hungarian Academy of Sciences (HAS) and at the Institute of Isotopes in Budapest as well as at the University of Debrecen and at Pannon University in Veszprém. The in-situ radiotracer “foil” method has been used at the Department of Radiochemistry of Pannon University for over two decades and combined with radiotracer (“foil” and “electrode lowering” methods) and voltammetric methods it offers a unique possibility to study sorption, electrocatalitical, corrosion and radioactive contamination processes. The available in-situ radiotracer methods are—among others—suitable for the examination of noble metal (mono-, polycrystalline) electrodes as well as metal and nonmetal structural surfaces (stainless steal, dye, powder samples).

The electrochemistry researches regarding heterogeneous solid/liquid systems also deal with the operating mechanisms of inhibitors with Cr-(VI)-contain and the role of Cr(III)-species in the corrosion mechanism of HSO_4^-/SO_4^{2-}-ions of the solid/liquid interfacial effects.

It is well known that the detailed surface qualities of noble metal electrodes (such as Au or Pt) are important to define and explain the electrosorption and electrocatalitic phenomena. Noble metal surfaces can be modified by adatoms (e.g. Zn, Ag, Cu, etc) in sub-monolayer, so the sorption, catalitic and corrosion behavior of the modified noble metal electrodes can be changed and improved. The development of electrocatalitic fuel cells form an essentially important part of the practical adoption of surface modified Pt and Au as catalysators. The underpotential deposition of metal ions has a significant role in the change of the catalytic quality and has a favourable influence on the sorption, corrosion and radioactive contamination processes.

In the light of the above facts the aims of the PhD research were the thorough study of the competitive, induced and enhanced anions adsorption on polycrystalline gold electrode and the understanding of the mechanism of related electrochemical processes. In my thesis I summarized the results of the in situ radiotracer and voltammetric measurements.

The main topics of the research are as follows:

1. Competitive adsorption of anions on polycrystalline gold electrode
2. The mechanism of Cr(VI)-reduction, the composition and the stability of the surface adsorption intermedier
3. The comparative analysis of the Adsorption of anions on polycrystalline gold electrode modified by Zn (Zn^{2+}-underpotential deposition) adatoms

Thesis

The important findings can summarized in the follows theses:

I. Competitive adsorption of anions on polycrystalline gold electrode

1. My results confirmed previous findings stating that a low pH-independent adsorption of HSO_4^-/SO_4^{2-}-ions can be detected on polycrystalline gold electrode in the studied pH-range (pH=0.0–4.5). The values and reproducability of the surface excess values are basically influenced by the competitive adsorption of polluting components present in low concentration (first of all Cl^--ions) in the solution by altering the surface of the gold (its purity and its roughness factor). Thus it is presumable that the HSO_4^--ions are adsorbed on the surface in the studied potential and pH-range.

2. Our studies verify that depending on the solution concentration of Cl^--ions and the applied electrode potentials, both adsorption and chemisorption processes of Cl^--ions take place on polycrystalline gold. In acidic solutions (pH=0.0–1.0) containing 1×10^{-4} mol dm^{-3} Cl^- on oxidfree gold surface the reversible adsorption of Cl^--ion can be measured. The surface excess values of the relative adsorption strength of Cl^--ions significantly exceed those of the of HSO_4^-/SO_4^{2-}-ions. At the same time clorocomplexes ($AuCl_2^-$, $AuCl_4^-$) are formed in the beginning range of the electrooxidation on polycrystalline gold in the chemisorption's process and the gold surface is dissolving. At more positive potentials parallel with the formation of gold-oxides surface clorocomplex formation is either decreasing or terminating that is the gold surface is passivized.

3. I determined the relative adsorption strength of studied anions on oxid-free polycrystalline gold electrode. The ranking is the following:
$Cl^- > H_2PO_4^- > HSO_4^-/SO_4^{2-} >> ClO_4^-$

II. The mechanism of Cr(VI)- reduction, the composition and the stability of the surface adsorption intermedier

1. I paid special attention to present a modified version of the in-situ radiotracer "foil" method, and to elaborate a novel detection and calculation procedure for the quantitative evaluation of the surface excess of radiolabeled Cr species via the measurement of the intensity of low energy X-rays (E=4.90 keV) emitted by ^{51}Cr.

2. I confirmed that the electroreduction of Cr(VI) particles presumably proceeds via a CE (chemical-electrochemical) mechanism to yield a gold surface covered with intermediate surface adlayer containing Cr(VI) species and added anions (HSO_4^-/SO_4^{2-}, ClO_4^-) at the potential range of E<1.20 V. I suggested that the extent and mechanism of adlayer formation are affected by the solution pH values. The maximum surface excess of Cr-containing species ($\Gamma_{pH=2.0}=1.6\times10^{-9}$ mol cm^{-2}; $\Gamma_{pH=0}=1.2\times10^{-9}$ mol cm^{-2}) as well as the molar ratio between the Cr species and HSO_4^-/SO_4^{2-}-ions ($m_{pH=0}\approx6$ at E=0.80 V; $m_{pH=2.0}\approx5$ at E=0.05 V) attest that the coverage of the gold surface with intermediate complexes does not exceed one monolayer.

III. Adsorption of anions on polycrystalline gold electrode modified by Zn (Zn^{2+}- underpotential deposition) adatoms

1. In ClO_4^--supporting electrolyte in pH≤2.0 range the presence of Zn^{2+}-ions in the solution phase does not influence the adsorption HSO_4^-/SO_4^{2-}- and Cl^--ions. At the same time at pH=4.5—during forming Zn adatoms—enhanced adsorption of HSO_4^-/SO_4^{2-}-ions can be detected. In the case of Cl^--ions, however, no similar effect can be detected. My additional studies conducted in 0.1 mol dm^{-3} KH_2PO_4 (pH=4.5) supporting electrolyte verified that the relative adsorption strength of studied anions on polycrystalline gold electrode modified by Zn adatoms is changing as follows:
$H_2PO_4^- > HSO_4^-/SO_4^{2-} > Cl^- >> ClO_4^-$.

2. To study Zn UPD I used $ZnCl_2$ labelled with ^{65}Zn in 0.1 mol dm^{-3} KH_2PO_4 (pH=4.5) supporting electrolyte. An in-situ radiotracer study could be based on the detection of the sum of secondary radiation (characteristic X-rays and/or bremsstahlung, Compton scattered and/or photo electrons etc.) induced by β^+-particles. It is practical to use such type of scintillator detector which is suitable for the detection of the indicated secondary electrons and of the characteristic X-rays and can be placed under the radiochemical cells. I used dE/dX plastic scintillator with a thickness of 0.1 mm to detect the induced secondary electrons ($E_{k\alpha}$=8.0 keV) emitted by ^{65}Zn. For these experiments I used low-energy characteristic X-rays by silicon semiconductor detector type XR 100T (AMPTEK, USA) attached to PCA-Multiport (Tennelec, USA) 8k multichannel analyser. Certainly it is simplier to use a dE/dX plastic scintillator because its surface is bigger and the efficiency of detection is more favourable. However, the surface excess values can only be detected with significant error, because only the combination of blended and secondary radiations can be detected and it changes by the sorption processes. The detector can not separate the primer β^+- and the inducated secondary radiation. In the light of the above facts I did not take notice of the calculation of surface excess values characteristic of Zn UPD. Consequently, the low intensity corresponds to higher surface excess (coverage of gold electrode by Zn adatoms). The maximum surface coverage (Θ is no more than 2.0 %) may only be estimated at 5×10^{-8} mol dm^{-3} Zn^{2+}-concentration, where the I values can be converted to surface concentrations by using the two evaluation methods described in literature.

3. The formation of Zn adatom is verified by defining time and potential dependence of Zn^{2+} adsorption labeled by ^{65}Zn. The Zn adatom forming on polycrystalline gold surface in 0.1 mol dm^{-3} KH_2PO_4 (pH=4.5) supporting electrolite can be detected already in 5×10^{-8} mol dm^{-3} Zn^{2+}-concentration by in-situ radiotracer method. If $\Gamma=2\times10^{-9}$ mol cm^{-2} surface excess value is equivalent with 1 monolayer Zn adatom coverage, the maximum coverage of gold surface does not exceed 2.0 %. There is a minimum concentration of Zn^{2+}-ions ($c=5\times10^{-4}$ mol dm^{-3}) in solutions at which the formation of Zn adatoms causes the onset of the hydrogen discharge to move to more negative potentials (in the range of $E\leq0.0$ V), indicating a site-blocking mechanism by the UPD of Zn. It is, however, plausible to assume that the coverage of the gold surface by Zn adatoms measured at solution concentrations of $c\geq5\times10^{-4}$ mol dm^{-3} does not exceed one monolayer.

Publication related to the PhD Thesis

Sientific publications

I. Reviewed articles in foreigne languages

1. K. Varga, I. Szalóki, L. Gáncs and R. Marczona: Novel application of an in-situ radiotracer method for study of the formation of surface adlayers in the course of Cr(VI) reduction on a gold electrode.
J. Electroanal. Chem. 524–525, 168–175 (2002).

2. R. Marczona, L. Gáncs, I. Szalóki and K. Varga: A novel radiotracer method to study the formation of surface adlayers in the course of Cr(VI) reduction on a gold electrode.
Czech. J. Physics 53, A429–A437 (2002).

3. R. Marczona and K. Varga: Adsorption phenomena on polycrystalline gold electrode modified by Zn adatoms.
J. Radioanal. Nucl. Chem. 269(1), 29–42 (2006)

II. Reviewed articles in Hungarian

1. Marczona R., Gáncs L., Szalóki I., Varga K.: A felületi rétegképződés in-situ radioizotópos nyomjelzéses vizsgálata polikristályos aranyelektródon Cr(VI)-ionokat tartalmazó vizes oldatokban.
Korróziós Figyelő, XLIII. Évf, 3. szám. 88–95, (2003)

2. Marczona R., Varga K.: Adszorpciós jelenségek Zn-adatomokkal módosított polikristályos aranyelektródon.
Korróziós Figyelő, XLIV. Évf, 6. szám. 195–205, (2004)

III. Abstracts of presentations and posters in foreign languages

1. K. Varga, I. Szalóki, L. Gáncs, R. Marczona: A novel radiotracer method to study the formation of surface adlayers in the course of Cr(VI) reduction on a gold electrode. International Conference on Electrified Interfaces (ICEI 2001), Wolfville (Nova Scotia), Canada, July 8–13, (2001)

2. R. Marczona, I. Szalóki, L. Gáncs, K. Varga: A novel radiotracer method to study the formation of surface adlayers in the course of Cr(VI) reduction on a gold electrode. SCK-CEN Belgian Research Centre, Mol, Belgium, September 25, (2002)

3. R. Marczona, K. Varga: Comparative In-situ Radiotracer and Voltammetric Study of the HSO_4^-/SO_4^{2-} and Cl^- Adsorption on a Polycrystalline Gold Electrode Modified by Zn Adatoms. 55th Annual Meeting of the International Society of Electrochemistry, Thessaloniki, Greece, 19–24 September, (2004)

IV. Abstracts of presentations and posters in Hungarian

1. Marczona R., Varga K.: ITDK Veszprém, Kémiai és Vegyipari Szekció (2000)

2. Gáncs L., Marczona R., Baradlai P., Szalóki I., Varga K.: Szimultán elektroszorpciós folyamatok vizsgálata aranyelektródon β-, illetve röntgensugárzás detektálásán alapuló in-situ radioizotópos nyomjelzéses módszerrel. „Őszi Radiokémiai Napok 2000” az MTA Radiokémiai Bizottság és MKE Radioanalitikai Szakcsoport tudományos ülése, Héviz, október 18–20, (2000)

3. Marczona R., Varga K.: XXV. OTDK Gödöllő, Kémiai és Vegyipari Szekció (2001)

4. Marczona R., Gáncs L., Szalóki I., Varga K.: A Cr(VI)-redukció mechanizmusának vizsgálata polikristályos aranyelektródon in-situ radioizotópos nyomjelzéses módszerrel. „Őszi Radiokémiai Napok 2001” az MTA Radiokémiai Bizottság és MKE Radioanalitikai Szakcsoport tudományos ülése, Mátraháza, október 17–19, (2001)

5. Marczona R., Gorjanácz Z., Varga K.: HSO_4^-/SO_4^{2-}-, és Cl^--ionok szimultán adszorpciójának vizsgálata Zn-adatomokkal módosított polikristályos aranyelektródon in-situ radioizotópos nyomjelzéses módszerrel. „Őszi Radiokémiai Napok 2002” az MTA Radiokémiai Bizottság és MKE Radioanalitikai Szakcsoport tudományos ülése, Gyula, 2002. október 16–18.

6. Marczona R., Gorjanácz Z., Varga K.: In situ radiokémiai és voltammatriás vizsgálatok a HSO_4^-/SO_4^{2-}-, Cl^--ionok szimultán adszorpciójának témakörében Zn-adatomokkal módosított polikristályos aranyelektródon. „Őszi Radiokémiai Napok 2003” az MTA Radiokémiai Bizottság és MKE Radioanalitikai Szakcsoport tudományos ülése, Balatonföldvár, október 8–10, (2003)

7. Marczona R., Varga K.: Anionok (HSO_4^-/SO_4^{2-} és Cl^-) kompetitív és megnövelt adszorpciója polikristályos aranyelektródon. „Őszi Radiokémiai Napok 2004” az MTA Radiokémiai Bizottság és MKE Radioanalitikai Szakcsoport tudományos ülése, Eger, október 13–15, (2004)