Measurement of adsorption rates of anions on Au(111) electrodes by impedance spectroscopy

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Abstract

We have measured impedance spectra on Au(111) electrode in aqueous perchlorate solutions containing specifically adsorbing anions (SO_4^{2-}, Cl^-, Br^- and I^-) of about 10^{-4} M concentrations at potentials where the dominant electrode process is the adsorption of the above anions. Accordingly, the impedance spectra have been analyzed in terms of the Frumkin–Melik-Gaykazyan adsorption impedance theory. With SO_4^{2-}, Cl^- we found the adsorption rates to be immeasurably high; with Br^- and I^- the apparent rate coefficients could be determined. For the halide anions this quantity increases in the order of $Cl^- > Br^- > I^-$; and rapidly decreases with increasing electrode potential and coverage. We attribute this change to the decrease of the occupancy related hindrance factor overcompensates the increase of the rate coefficient. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The specific adsorption of ions onto metal electrodes has been investigated by various groups for many years. Most of these studies have dealt with the thermodynamic and structural aspects of the adsorption—the objective was to determine the surface coverages of a particular ion on a particular surface and/or to characterize the structure of the adlayer. Kinetic studies have been much more scarce; in contrast to the numerous redox kinetics information available, the adsorption–desorption kinetics is much less known.

The purpose of the present study was to repeat and extend an earlier series of measurements [1]: 6 years ago bromide adsorption on single crystalline gold electrodes was studied by one of us. Since certain kinetic features of that system were found to be strange, we repeated the measurements with improved accuracy and performed the measurements also with other anions.

In principle, electrochemical adsorption kinetics can be studied by transient and/or perturbation methods; as it is common with kinetic studies, clean and well-defined conditions are required. More specifically, kinetics can be measured by using impedance spectroscopy, on well-defined single crystalline surfaces. In the present paper we show the results of electrochemical impedance measurements carried out on an Au(111) single crystal electrode in aqueous perchlorate solutions containing sulfate and halide (bromide, iodide, chloride) anions. The spectra are analyzed in terms of a somewhat modernized form of the Frumkin–Melik-Gaykazyan adsorption impedance theory developed step-by-step by Ershler [2], Frumkin and Melik-Gaykazyan [3], and Lorenz and Möckel [4]. Although modernized versions of the theory can be found in, e.g. [5,6], to emphasize the main points we also present our version of the theory in the Appendix A.

2. Methods

The experimental set-up (instruments and software for cyclic voltammetry (CV), impedance measurements),

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the cell, chemicals, and all the experimental procedures were the same or very similar to those used in our previous study of Au single crystals [1]; however, the improved cleanliness due to the altered cleaning procedures enabled longer measurement series. Now we could perform measurement series of about 2 h, which was a sufficiently long time to measure 10–40 impedance spectra as function of potential without re-annealing the electrode. The measurements were carried out in 0.1 M HClO$_4$ solution containing 0.1–1 mM K$_2$SO$_4$, KCl, KBr, or NaI (in the last case with 0.1M KClO$_4$ base electrolyte). All chemicals were of the highest purity available.

Like in [1], for the analysis of the measured impedance spectra we used the adsorption impedance theory predicting the equivalent circuit shown in Fig. 1; the parameters of this circuit were fitted to the measured spectra by a non-linear least squares program. After performing the curve fitting, little if any systematic deviations of the measured and calculated spectra could be observed indicating that the fitting function was adequate; in general, the χ^2 values (residual mean squares) of the fits were between 10^{-5} and 10^{-4}, that is, the average deviation between measured and fitted points was less than 1%.

There is one methodological improvement which deserves mentioning: After having prepared the cell and the electrode, we have usually measured many (20–40) impedance spectra as function of potential, and then these were fitted by the equivalent circuit of Fig. 1. All elements but the solution resistance depended on potential; the solution resistance being a 'common'

quantity, is constant or slowly increasing in time due to the slow evaporation of the electrolyte (due to which the meniscus height slightly increased in time). To take into account the common origin of R_s we applied the following procedure: First we fitted all five parameters (including R_s) of the circuit of Fig. 1 to the spectra, which usually yielded a constant or a linear $R_s(t)$ time-function. Next we fitted a straight line to this $R_s(t)$ function; from the fitted parameters we determined an 'exact' value of R_s for each spectra. In the last step we re-fitted each spectra with fixed R_s and by the other four parameters. This procedure somewhat improved the accuracies of those parameters which are relevant at the high frequency end of the spectra.

The measured spectra, just as in [1], are represented graphically throughout this work by calculating and plotting the $C(\omega) = Y(\omega)/(i\omega) = 1/([Z(\omega) - Z(\omega \to \infty)]A_e i\omega)$ complex function, where ω, $Z(\omega \to \infty) = R_s$, A_e, and i are the angular frequency, the solution resistance, the electrode area, and the imaginary unit, respectively. Due to its physical meaning $C(\omega)$ is termed the 'interfacial capacitance' and, being a complex quantity, can be plotted in complex representation (on a Nyquist-plot, being analogous to the Cole–Cole plot used in context of dielectrics). According to the adsorption impedance theory (see the Appendix A) the interfacial capacitance spectrum, $C(\omega)$, is of the form:

$$C(\omega) = \frac{1}{i\omega(Z(\omega) - R_s)}$$

$$= C_{dl} + \frac{C_{ad}}{1 + \sigma_{ad}C_{ad}\sqrt{i\omega} + R_{ad}C_{ad}i\omega} \quad (1)$$

(cf. Eq. (19)) where the quantities are defined in the legend of Fig. 1. Provided the adsorbate concentration is in the 0.1–1 mM range, the capacitance spectra in complex representation are semicircles or depressed arcs for the limiting cases (Fig. 1); if the adsorbate concentration is much higher or lower than this concentration range then the spectra shrink into single points at C_{ad} or C_{dl}, respectively. This is why for the determination of the kinetic parameters solutions of adsorbate concentrations of 0.1 and 0.2 mM were used. One can obtain the best accuracy of the fitted rate coefficients with these concentrations; the setup used in the present study made possible the determination of rate coefficients in the 10^{-3}–1 cm s^{-1} range.

Fig. 1. Complex plots of the $C(\omega)$ function (defined by Eq. (1)) of the circuit of the inset. C_{dl}, C_{ad}, and R_{ad}, stand for double layer and adsorption capacitances, and adsorption resistance, respectively, σ_{ad} is the coefficient of the Warburg impedance, W_{ad}, defined by $Z(W_{ad}) = \sigma_{ad}(i\omega)^{-1/2}$, and R_s is the solution resistance. Semicircle and the depressed arcs: limiting cases of slow and fast (diffusion controlled) adsorption, respectively; skewed arc: intermediate case, mixed kinetics.

3. Results

To demonstrate the cleanliness of the system and measurement accuracy, we show a voltammogram, impedance and capacitance spectra (Fig. 2(a)) measured on Au(111) in the base electrolyte (0.1 M HClO$_4$). All these plots confirm that the Au(111)/0.1M HClO$_4$
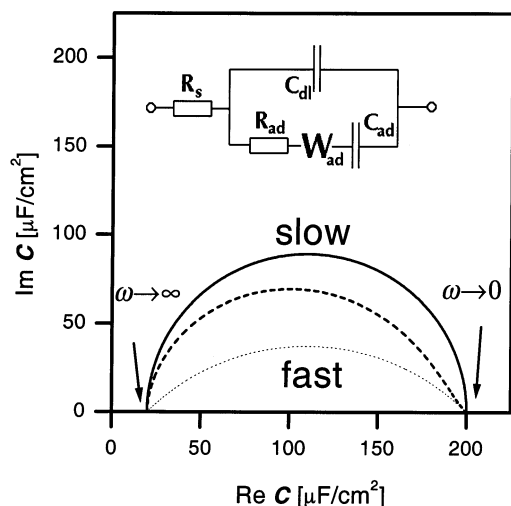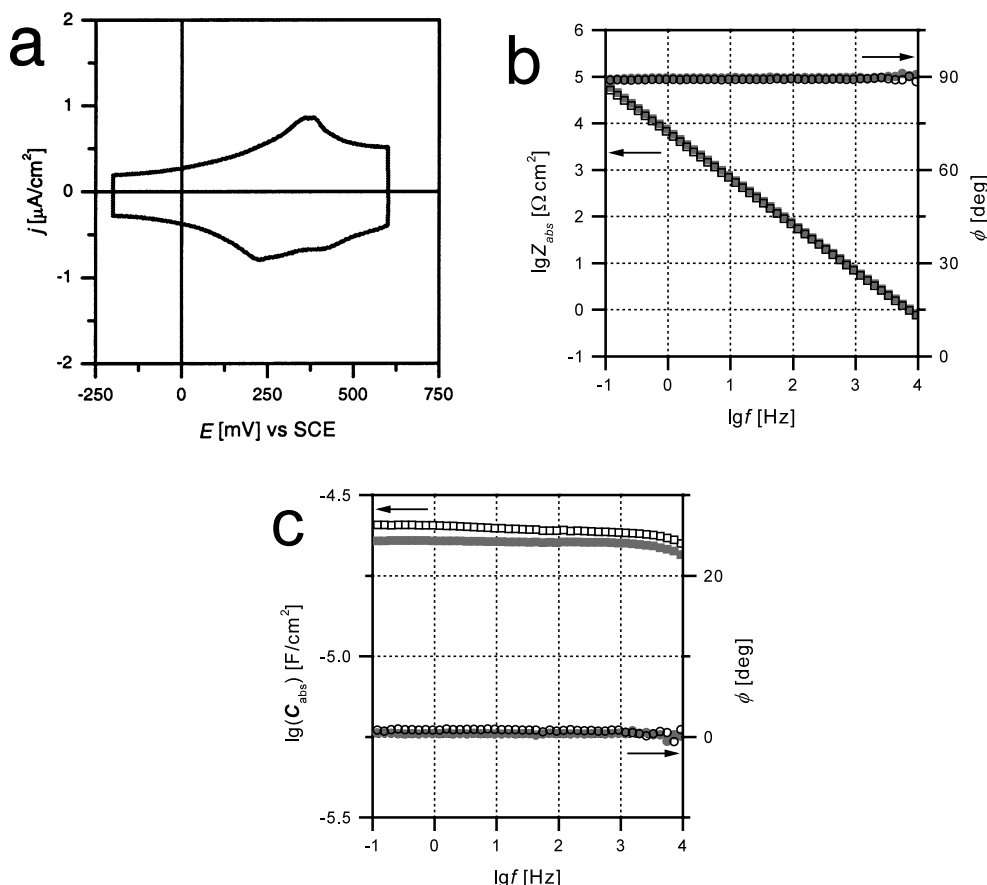
Fig. 2. (a) Cyclic voltammogram (sweep rate 10 mV s^{-1}) of Au(111) in 0.1 M HClO$_4$ solution. (b) Impedance spectra (with solution resistance subtracted) of Au(111) in 0.1 M HClO$_4$ solution (full symbols, ■●) and in 0.1 M HClO$_4$ solution containing 0.1 mM K$_2$SO$_4$ (open symbols, □○), at $E = -0.2$ V vs. SCE (squares: magnitudes, circles: phase angles). (c) Capacitance representation of the impedances of Fig. 1(a).

interface is capacitive, no Faradaic current is flowing. The $C(\omega)$ function is virtually frequency-independent: if it is approximated by a constant phase element, the exponent, α, is 0.997[1]. Similarly, we observe almost ideal capacity ($\alpha = 0.992$) also with sulfate containing solution if the potential is sufficiently cathodic to suppress sulfate adsorption (Fig. 2(b) and (c)).

With solutions containing specifically adsorbing ions (SO$_4^{2-}$, Cl$^-$, Br$^-$ and I$^-$) we observe the following changes.

The currents of the voltammograms (Fig. 3(a) and Fig. 6(a)) markedly increase; however, the current loop remains by and large symmetrical with respect to the potential axis indicating that the Faradaic current is much smaller (in fact, negligibly small) than the charging current. There appear peak pairs due to phase transitions of the surface (associated with surface reconstruction and two-dimensional phase transitions of the adlayers); however, these processes and peaks are

not important in the context of the present communication and, therefore, are further not mentioned.

Interfacial capacitances, plotted in the complex plane are of arc shapes; accordingly, the impedances can be well fitted with Eq. (1) with finite values of the adsorption related impedances.

In the case of Cl$^-$ and SO$_4^{2-}$ the spectra are depressed arcs at each potentials measured (Figs. 3 and 4), indicating that the adsorption of Cl$^-$ and SO$_4^{2-}$ is so fast as to making kinetics to be diffusion-controlled in the complete potential range of adsorption. Accordingly, the fitting procedures yield R_{ad} which do not differ significantly from zero. The self-consistency of the data processing can be tested by calculating the diffusion coefficient, D, from the Warburg coefficient obtained by the curve fitting, using Eq. (29) and the electrosorption valency data of Ref. [7]. A value of $D = 1.8 \pm 0.5 \times 10^{-5}$ cm^2 s^{-1} has been obtained being in good agreement with the literature data (2.03×10^{-5} cm^2 s^{-1}, Ref. [8]; note that we found similar agreement for all the other adsorbate anions of the present study: values always around 2×10^{-5} cm^2 s^{-1} have been obtained).

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[1] To the best of our knowledge, this is the 'best' double layer capacitance ever found in an electrochemical system.
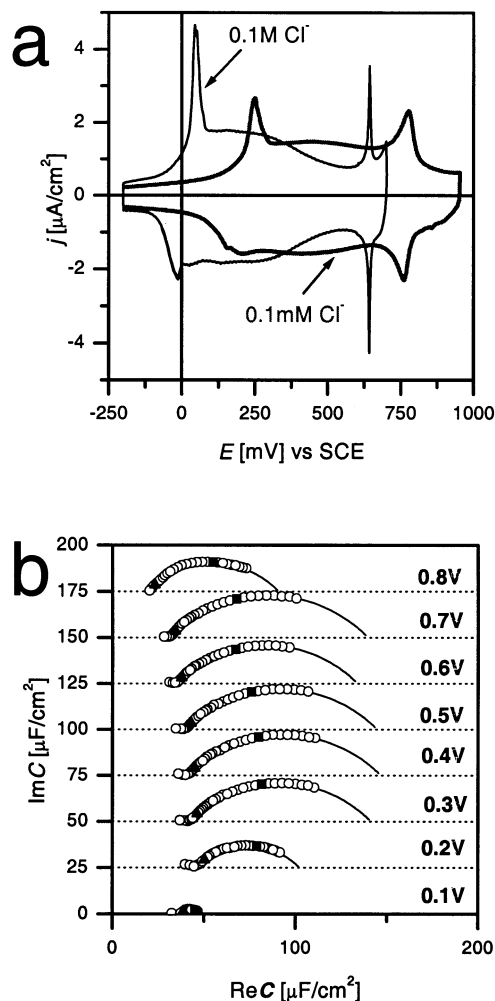
Fig. 3. (a) Cyclic voltammograms (sweep rate 10 mV s^{-1}) of Au(111) in 0.1 M HClO$_4$ solution containing 0.1 mM (dotted line), and 100 mM (thick solid line) KCl. (b) Capacitance spectra of Au(111) in 0.1 M HClO$_4$ solution containing 0.1 mM KCl at potentials indicated. Frequency range 10 kHz–1 Hz; ■: 10 Hz, ●: 1 kHz; solid lines: fitted curves. The spectra are shifted vertically for clarity.

In the case of Br$^-$ and I$^-$ the capacitance spectra are depressed arcs at cathodic potentials and change to asymmetric, 'skewed' arcs when changing the potential in positive direction (Figs. 5 and 6). Accordingly, in the latter potential range the curve fitting procedure yielded significantly non-zero R_{ad} values. From the fitted R_{ad} values, also using the electrosorption valency data of [7], apparent rate coefficients, $k_{ad}f_{ad}$ values were calculated using Eq. (28). These are shown as function of potential in Fig. 7(a). The $k_{ad}f_{ad}$ values depend on the concentration of the adsorbate, due to that the occupancy related hindrance factor f_{ad} depends the concentration through the coverage: $f_{ad} = f_{ad}(\theta) = f_{ad}(\theta(c))$. In order to eliminate the concentration dependence, we have re-plotted the data by changing the abscissa (bottom scale of Fig. 7(b)) to surface excess using the $\Gamma(E)$ and $\gamma(E)$ data of Refs. [7]; and considering also Eq. (31). By this scale
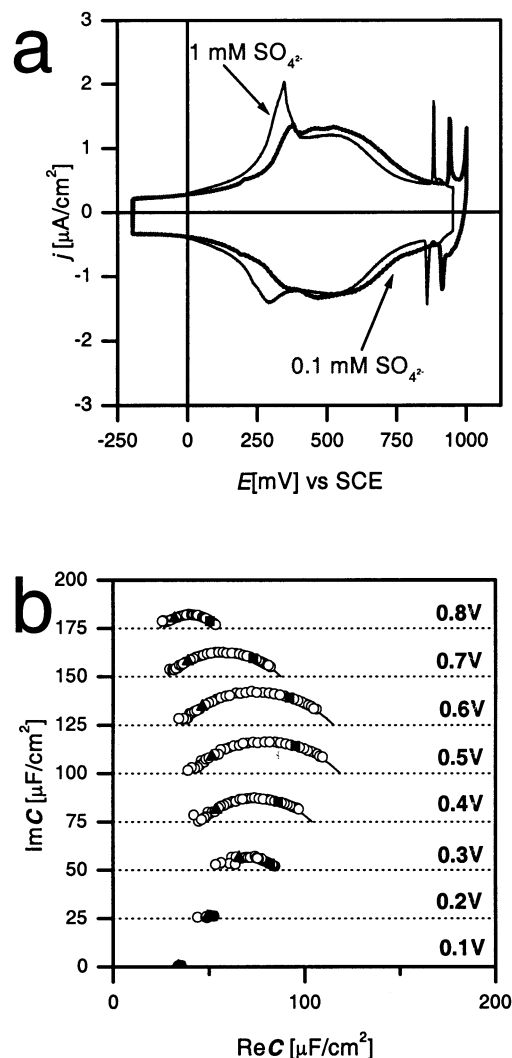
Fig. 4. (a) Cyclic voltammograms (sweep rate 10 mV s^{-1}) of Au(111) in 0.1 M HClO$_4$ solution containing 0.1 mM (dotted line), 1 mM (thin solid line) K$_2$SO$_4$. (b) Capacitance spectra of Au(111) in 0.1 M HClO$_4$ solution containing 0.1 mM K$_2$SO$_4$ at potentials indicated. Frequency range 10 kHz–1 Hz; ■: 10 Hz, ●: 1 kHz; solid lines: fitted curves.

transformation the concentration dependence vanishes. For illustration, we also specify coverage as a relative quantity θ_r defined as the ratio of the number of adsorbed ions and of surface gold atoms (see the top scale of Fig. 7(b)).

4. Discussion

The apparent rate coefficients are in the range of 10^{-3}–1 cm s^{-1} (see Fig. 7), with Br$^-$ and I$^-$ ions at sufficiently high coverages, or are larger than 1 cm s^{-1}, as with Br$^-$ and I$^-$ ions at low coverages and with SO$_4^{2-}$ and Cl$^-$ at any coverages. From these data we conclude that the apparent rate coefficients, $k_{ad}f_{ad}(\theta)$ increase in the Cl$^-$ > Br$^-$ > I$^-$ order, SO$_4^{2-}$ adsorption is immeasurably fast just as of chloride. However, for
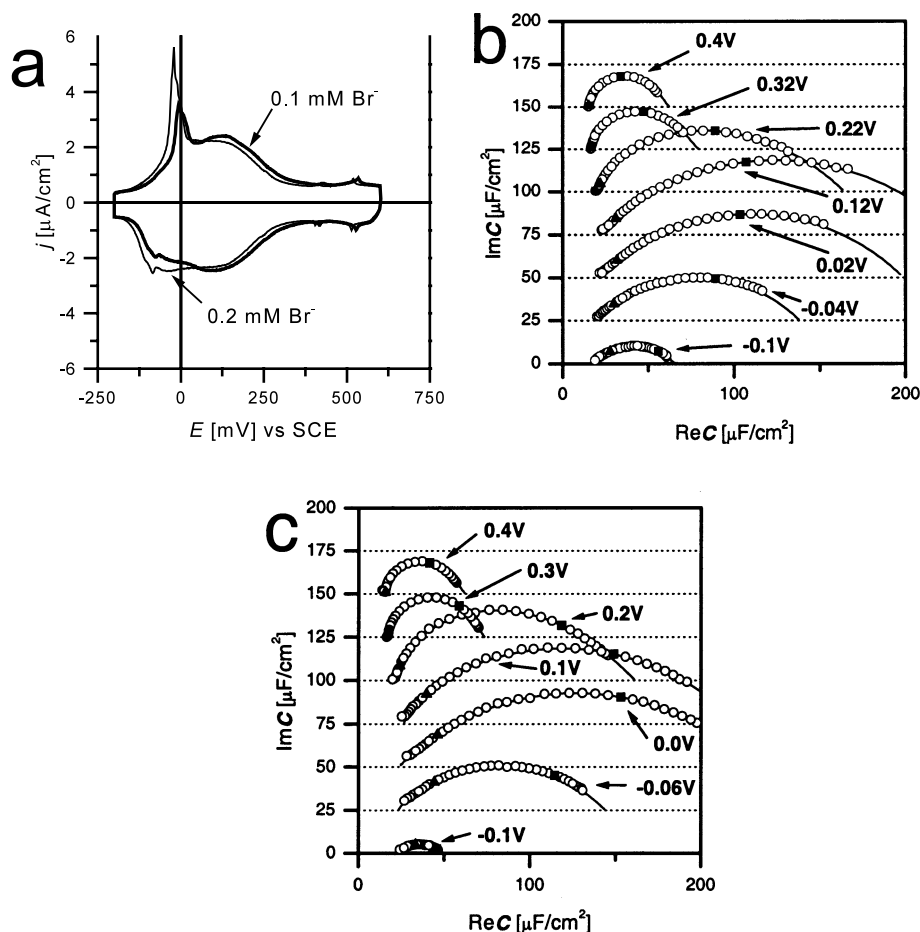
Fig. 5. (a) Cyclic voltammograms (sweep rate 10 mV s^{-1}) of Au(111) in 0.1 M HClO$_4$ solution containing 0.1 mM and 0.2 mM KBr. (b) Capacitance spectra of Au(111) in 0.1 M HClO$_4$ solution containing 0.1 mM KBr at potentials indicated. Frequency range 10 kHz–1 Hz; ■: 10 Hz, ●: 1 kHz; solid lines: fitted curves. The spectra are shifted vertically for clarity. (c) Same as (b), in solution containing 0.2 mM KBr.

the k_{ad} rate coefficient we cannot establish such an order. This could be done only if the apparent rate coefficients were compared at constant $f_{ad}(\theta)$—rather than at constant θ (along a vertical line on Fig. 7(b)); or, if the $k_{ad}f_{ad}(\theta)$ values at low θ were compared (since if $\theta \rightarrow 0, f_{ad}(\theta) \rightarrow 1$).

As is seen in Fig. 7(a), all apparent rate coefficients are decreasing with increasing potential. This finding has interesting consequences.

As we emphasized in the Appendix A, for the derivation of Eq. (28) there is no need to assume any potential dependence of k_{ad} and k_d. Nevertheless, it is reasonable to assume a potential dependence between the negatively charged anions and the electrode surface, therefore, only for the purpose of interpreting Fig. 7, we follow Berzins and Delahay [9] and assume exponential potential dependences, i.e. $k_{ad} = k_{ad}^0 \exp(-\alpha zFE/RT)$ and $k_d = k_d^0 \exp(+\beta zFE/RT)$ where α and β are empirical constants, $z = -1$ for the halide ions and the other symbols have their usual meaning. Note that such dependences would yield exponentially increasing and decreasing adsorption and desorption rates, respec-

tively, as function of potential if the coverage effect was ignored. However, Fig. 7(a) shows an exponentially decreasing—rather than increasing—apparent adsorption rate. This can be explained only by assuming that the decrease of $f_{ad}(\theta)$ overcompensates the increase of k_{ad}. This explanation is reasonable if we consider that the θ_r values of 0.3–0.4 indicate almost fully covered surface taking also into account that the bromide or iodide anions are much larger than the gold atoms (the ionic radii of these halide ions and of the atomic radius of gold are 1.96, 2.20 and 1.46 Å, respectively, that is, a full monolayer corresponds to $\theta_r \approx 0.5$).

5. Summary and conclusions

We have measured impedance spectra on Au(111) electrode in perchlorate solutions containing specifically adsorbing anions (SO$_4^{2-}$, Cl$^-$, Br$^-$ and I$^-$) of about 10^{-4} M concentrations at potentials where no Faradaic current is flowing and the dominant electrode process is the adsorption of the above anions. Accordingly, the
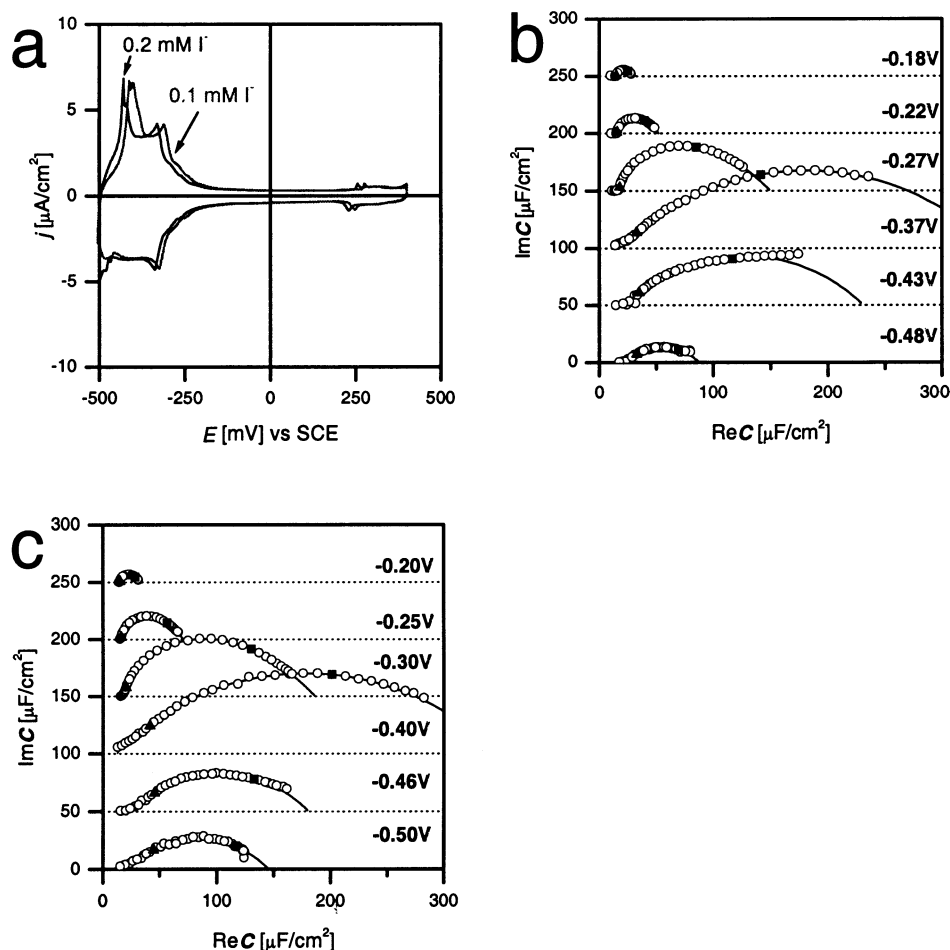
Fig. 6. (a) Cyclic voltammograms (sweep rate 10 mV s^{-1}) of Au(111) in 0.1 M KClO$_4$ solution containing 0.1 mM and 0.2 mM KI. (b) Capacitance spectra of Au(111) in 0.1 M KClO$_4$ solution containing 0.1 mM KI at potentials indicated. Frequency range 10 kHz–1 Hz; ■: 10 Hz, ●: 1 kHz; solid lines: fitted curves. The spectra are shifted vertically for clarity. (c) Same as (b), in solution containing 0.2 mM KI.

impedance spectra have been analyzed in terms of the somewhat modified form of the Frumkin–Melik-Gay-kazyan adsorption impedance theory yielding-among others-the adsorption resistance. Unless this quantity was zero, the apparent rate coefficient of the adsorption could be determined.

In the case of sulfate and chloride anions adsorption resistance was found to be zero (within the accuracy limits) everywhere in the potential range studied; that is, the apparent rate coefficient was unmeasurably high. In contrast, with bromide and iodide, there exist potential ranges in which the adsorption resistance is definitely non-zero, thereby allowing us to calculate the apparent rate coefficients of the ion adsorption. This quantity is given as function of electrode potential and of surface excess or coverage in Fig. 7.

The apparent rate coefficient increases among the halide anions in the order Cl$^-$ > Br$^-$ > I$^-$; and rapidly decreases with increasing electrode potential and cover-age—we attribute this change to the decrease of the

occupancy related hindrance factor $f_{ad}(\theta)$ overcompensates the increase of the rate coefficient k_{ad}.

Appendix A: Adsorption impedance

In general, differential capacity of a metal/electrolyte interface is defined as $C_{dl} = dq^M/dE$, where q^M is the excess charge of the metal. This is a definition based on
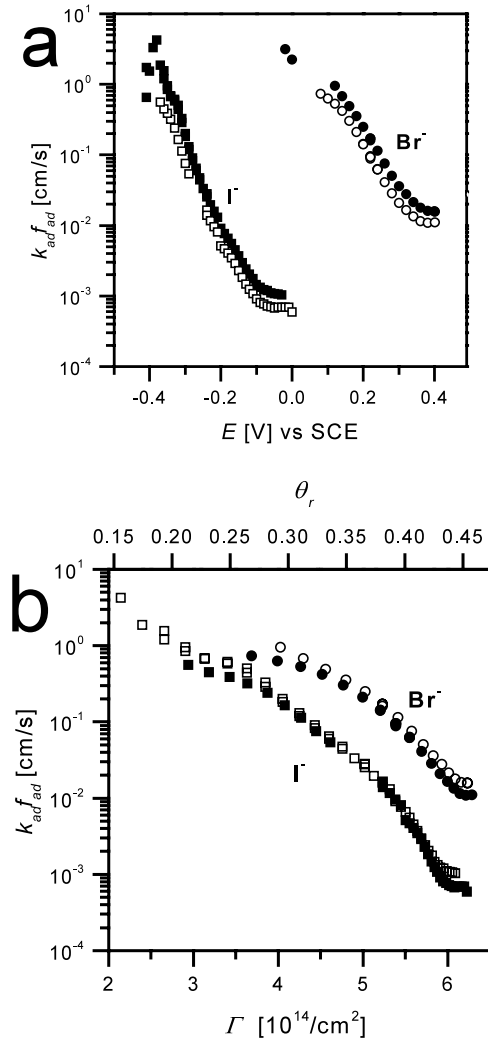
Fig. 7. Apparent rate coefficients of bromide and iodide ions on Au(111) as function of potential (a) and as function of surface excess and of coverage (b). Solutions: ■, □: 0.1 and 0.2 mM iodide in 0.1 M KClO$_4$, respectively; ●, ○: 0.1 and 0.2 mM bromide in 0.1 M HClO$_4$, respectively. Coverage, θ_r is defined as the ratio of the number of adsorbed ions and of surface gold atoms.

electrostatics, and as such, reflects none of the temporal or frequency behavior of the double layer. This latter dependences will be analyzed in this section as follows.

According to our views on double layer and adsorption, q^M depends on E firstly directly, and secondly indirectly, through the surface excess of the adsorbate, Γ; i.e. in our models we assume a $q^M = q^M(E, \Gamma(E))$ form. Hence we can define double layer capacity in two ways: Either by $C_{dl,\Gamma} = (\partial q^M / \partial E)_\Gamma$ or by $C_{dl} = dq^M / dE$. The first definition refers to a state, which is frozen from the point of adsorption, whereas the second is the total capacity. Therefore, irrespectively of the impedance model of the interface, $C_{dl,\Gamma}$ and C_{dl} can be identified as C_{HF} and C_{LF}, respectively, and $C_{ad} = C_{LF} - C_{HF}$.

To determine C_{ad}, we assume a one-step adsorption–desorption (desad) process of a species (uncharged or charged) with a net rate v normalized to unit area. This changes the coverage as

$$\frac{d\Gamma}{dt} = v(E, c_s, \Gamma) = v_{ad} - v_d \tag{2}$$

where v_{ad} and v_d are the rates of adsorption and desorption, respectively, and c_s is the concentration of the absorbed species at the electrode surface just outside of the double layer. Note that at this point we do not assume any concrete form of the $v(E, c_s, \Gamma)$ function. The current, related to the adsorption is expressed as

$$I = \frac{dq^M}{dt} = -\gamma F \frac{d\Gamma}{dt} \tag{3}$$

where γ is the electrosorption valency [10] defined by

$$\gamma = \frac{-1}{F} \frac{dq^M}{d\Gamma} = \frac{1}{F} \frac{d\mu_{ad}}{dE} \tag{4}$$

In what follows, we assume adsorption equilibrium with a small sinusoidal perturbation around the equilibrium, that is $\delta\Gamma(t) = \Gamma(t) - \Gamma_e = \bar{\Gamma}\exp(i\omega t)$; $\delta E(t) = E(t) - E_e = \bar{E}\exp(i\omega t)$; $\delta c_s(t) = c_s(t) - c_{s,e} = \bar{c}_s\exp(i\omega t)$ where the index e refers to the equilibrium state, and $c_s = c_b$, the bulk concentration and the overlined quantities are complex amplitudes. Due to the small perturbation, we can expand Eq. (2) and drop all but linear terms to obtain

$$\frac{d\delta\Gamma(t)}{dt} = \frac{\partial v}{\partial E}\delta E(t) + \frac{\partial v}{\partial c_s}\delta c_s(t) + \frac{\partial v}{\partial \Gamma}\delta\Gamma(t)$$
$$= v_E\delta E(t) + v_c\delta c_s(t) + v_\Gamma\delta\Gamma(t) \tag{5}$$

Introducing the periodic functions

$$i\omega\bar{\Gamma} = v_E\bar{E} + v_c\bar{c}_s + v_\Gamma\bar{\Gamma} \tag{6}$$

In case of semi-infinite planar diffusion there exists a connection [11] between c_s and the diffusional flux of the adsorbate, Φ; for the perturbation terms it takes the following form:

$$\bar{c}_s = \frac{\bar{\Phi}}{\sqrt{i\omega D}} \tag{7}$$

where D is the diffusion coefficient of the ion. Due to continuity $\Phi = d\Gamma/dt$, hence

$$\bar{c}_s = \frac{i\omega\bar{\Gamma}}{\sqrt{i\omega D}} = \sqrt{\frac{i\omega}{D}}\bar{\Gamma} \tag{8}$$

In the case of periodic perturbation Eq. (3) can be rewritten in the following form:

$$\bar{I} = -\gamma F i\omega\bar{\Gamma} \tag{9}$$

Eqs. (6)–(9) together yield:

$$\frac{\bar{I}}{-\gamma F}\left(1 - \frac{v_\Gamma}{i\omega} - \frac{v_c}{\sqrt{i\omega D}}\right) = v_E \bar{E} \tag{10}$$

Since the impedance $Z(\omega) \equiv \bar{E}/\bar{I}$, we obtain an impedance of a series RWC circuit:

$$Z \equiv \frac{\bar{E}}{\bar{I}} = R_{ad} + \frac{\sigma_{ad}}{\sqrt{i\omega}} + \frac{1}{C_{ad}i\omega} \tag{11}$$

with the parameters

$$R_{ad} = \frac{-1}{\gamma F v_E} \tag{12}$$

$$\sigma_{ad} = \frac{-1}{\gamma F \sqrt{D}} \frac{v_c}{v_E} \tag{13}$$

$$C_{ad} = \gamma F \frac{v_E}{v_\Gamma} \tag{14}$$

C_{ad}, R_{ad}, and σ_{ad} (or some combinations of these) are the three parameters which can be directly determined from the impedance spectra. We can obtain the partial derivatives of v by expressing them from the above equations yielding:

$$v_c = \sqrt{D}\frac{\sigma_{ad}}{R_{ad}} \tag{15}$$

$$v_\Gamma = \frac{-1}{C_{ad}R_{ad}} \tag{16}$$

$$v_E = \frac{-1}{\gamma F R_{ad}} \tag{17}$$

Note that at the equilibrium $v = 0$; whereas its partial derivatives differ from zero.

For the sake of completeness we note that by taking into consideration the high frequency capacitance and the solution resistance as well we get the full electrode impedance as:

$$Z(\omega) = R_s + \cfrac{1}{i\omega C_{HF} + \cfrac{1}{R_{ad} + \cfrac{\sigma_{ad}}{\sqrt{i\omega}} + \cfrac{1}{i\omega C_{ad}}}} \tag{18}$$

and the 'frequency normalized interfacial admittance', $Y/(i\omega)$:

$$C(\omega) = \frac{1}{i\omega(Z(\omega) - R_s)}$$

$$= C_{HF} + \frac{C_{ad}}{1 + \sigma_{ad}C_{ad}\sqrt{i\omega} + R_{ad}C_{ad}i\omega} \tag{19}$$

At high frequency the second term approaches zero, thus the high frequency limit equals with the double layer capacity. ($C(\omega \to \infty) = C_{HF} = C_{dl}$); at low frequencies the sum of the double layer capacity and

adsorption capacity can be measured ($C(\omega \to 0) = C_{LF} = C_{dl} + C_{ad}$).

Now we specify the rate equations by assuming simple (still fairly general) equations for the adsorption and desorption steps. We define the following quantities: $\theta = \Gamma/\Gamma_{max}$ is the coverage; $f_{ad}(\theta)$ and $f_d(\theta)$—occupancy related factors—are some monotonously decreasing and increasing function of θ, respectively, (in the simplest case $f_{ad} = 1 - \theta$, and $f_d = \theta$; corresponding to Langmuirian adsorption). We specify the values of these functions in the limiting cases only: $f_{ad}(\theta \to 0) = 1$; $f_{ad}(\theta \to 1) = 0$; $f_d(\theta \to 0) = 0$; $f_d(\theta \to 1) = 1$. Using these we specify the rate equations as follows:

$$v = v_{ad} - v_d \quad v_{ad} = k_{ad}c_s f_{ad}(\theta) \quad v_d = k_d f_d(\theta) \tag{20}$$

$$v = k_{ad}c_s f_{ad}(\theta) - k_d f_d(\theta) \tag{21}$$

where coefficients k_{ad} and k_d are the rate coefficients of adsorption and desorption, respectively. The $k_{ad}f_{ad}(\theta)$ and $k_d f_d(\theta)$ products will be denoted as apparent rate coefficients. The $k_{ad}f_{ad}(\theta)$ is given in cm s^{-1} units and as such, expresses the rate by which the anions adsorb onto the surface, which is partially covered. k_{ad} (also in cm s^{-1} units) is the rate of the process in which the anions adsorb onto a completely free surface.

The partial derivatives of Eqs. (15)–(17) thus are of the form:

$$v_c = \sqrt{D}\frac{\sigma_{ad}}{R_{ad}} = k_{ad}f_{ad}(\theta) \tag{22}$$

$$v_\Gamma = \frac{-1}{C_{ad}R_{ad}} = k_{ad}c_s\frac{\mathrm{d}f_{ad}(\theta)}{\mathrm{d}\Gamma} - k_d\frac{\mathrm{d}f_d(\theta)}{\mathrm{d}\Gamma} \tag{23}$$

$$v_E = \frac{-1}{\gamma F R_{ad}} = \frac{\mathrm{d}k_{ad}}{\mathrm{d}E}c_s f_{ad}(\theta) - \frac{\mathrm{d}k_d}{\mathrm{d}E}f_d(\theta) \tag{24}$$

We stress that c_s, k_{ad}, k_d, f_{ad}, and f_d are DC quantities; in the subsequent equations we shall employ the steady state condition of $c_{s,e} = c_b$.

The apparent rate coefficient of the adsorption can be directly determined using Eq. (22). Unfortunately, this type of analysis, can be done in fairly narrow potential ranges where the capacitance spectra are of skewed ark shape. There is, however, another way of analysis, based on the following lines of thoughts.

According to the irreversible thermodynamics close to the adsorption equilibrium $\delta v = K\delta(\mu_{ad} - \mu_b)$ where $\mu_{ad} = \mu_{ad}(E, \Gamma)$ and $\mu_b = \mu_b(c_b) = \mu_b^0 + RT\ln(c_b)$ are the chemical potential of the adsorbate in the adsorbed state and the solution bulk, respectively, and K is a proportionality constant [6]. Taking also into account that in adsorption equilibrium $c_s = c_b$, and, the partial derivative in the lhs of Eq. (22) are expressed as:

$$v_c = -K\left(\frac{\partial \mu_b}{\partial c_s}\right)_{E,\Gamma} = -K\left(\frac{\partial \mu_b}{\partial c_b}\right)_{E,\Gamma} = -KRT\frac{1}{c_b} \tag{25}$$

and taking also into account the definition equation of γ (Eq. (4)):

$$v_E = K\left(\frac{\partial \mu_{ad}}{\partial E}\right)_{E,\Gamma} = K\gamma F \tag{26}$$

Combining Eqs. (15), (17), (25) and (26), we obtain:

$$\sigma_{ad} = \frac{1}{-\gamma F\sqrt{D}} \frac{v_c}{v_E} = \frac{1}{-\gamma F\sqrt{D}} \frac{-KRTc_b^{-1}}{K\gamma F}$$

$$= \frac{RT}{\gamma^2 F^2 \sqrt{D} c_b} \tag{27}$$

Together with Eq. (22) we obtain that:

$$k_{ad} f_{ad}(\theta) = \frac{RT}{\gamma^2 F^2 c_b R_{ad}} \tag{28}$$

Note that—in contrast with earlier derivations, e.g. [9]—we did not need to assume any potential dependence of the adsorption rate.

Other expressions can also be obtained from the above equations. For example, the diffusion coefficient can be expressed from Eq. (27) yielding:

$$D = \left(\frac{RT}{\gamma^2 F^2 c_b \sigma_{ad}}\right)^2 \tag{29}$$

Eq. (29) allows us to determine either the diffusion coefficient or the electrosorption valency.

A further equation is employed in this paper: Assume adsorption equilibrium, that is, $\mu_{ad} = \mu_b$; adsorbate coverage depends on potential, E and bulk concentration c_b. We now show how to change E and c_b simultaneously while keeping constant coverage. In this case $\mu_{ad} = \mu_{ad}(E)$ and $\mu_b = \mu_{ad}(c_b) = \mu_b = \mu_b^0 + RT\ln(c_b)$ thus for constant coverage

$$\frac{\partial \mu_{ad}}{\partial E}\mathrm{d}E = \frac{\partial \mu_b}{\partial c_b}\mathrm{d}c_b \qquad \text{hence} \qquad \gamma F\mathrm{d}E = RT\frac{1}{c_b}\mathrm{d}c_b \tag{30}$$

Thus, if bulk concentration is changed from c_1 to c_2, then E must be changed by:

$$\Delta E = (RT/\gamma F)\ln(c_2/c_1) \tag{31}$$

for having same coverage.

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