Coulostatic pulse relaxation at the TiO₂ (single crystal)/electrolyte solution interface

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Coulostatic Pulse Relaxation at the TiO_2 (Single Crystal)/Electrolyte Solution Interface

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The relaxation of coulostatic pulses at the TiO_2 (single crystal)/electrolyte solution interface is analyzed in terms of an equivalent circuit which distinguishes among the capacity of the semiconductor space charge, the capacity of surface states, two adsorption capacities, and a diffusion process in the liquid phase. The semiconductor space charge capacity is characterized by a Mott-Schottky-like dependence on the potential drop over the interface; it can be used to calculate the donor concentration and the flat band potential. The latter shifts to more negative values (toward SCE) with increasing pH. © 1987 Academic Press, Inc.

1. INTRODUCTION

In previous papers (1) (see also Ref. (2)), we presented experimental data on surface charge and zeta potentials of TiO_2 in aqueous solutions. These were analyzed in terms of the site binding model; some problems were exposed in the usual assumptions introduced in working with this model. The present paper aims at elucidating other aspects of the TiO_2 /electrolyte solution interface, viz., the complex impedance of this interface. Analysis of the impedance supplies insight into the processes occurring near such an interface, e.g., on pair formation during coagulation.

Measurements of the impedance of an interface solid/electrolyte solution are frequently performed by phase-sensitive detection. However, such measurements over a wide frequency range require a continuous perturbation of the interface by ac signals. In order to avoid this, we applied a transient technique; in this method the system is subjected to only one small perturbation. Among the alternatives (galvanostatic (3), potentiostatic (4) or coulostatic (5, 6) pulses) we used the latter be-

cause of its lack of sensitivity to ohmic potential drop (13).

2. EXPERIMENTAL

2.1. TiO_2 (Rutile) Single Crystals

(a) *Ex Atomergic, employed for cutting wafers exposing the (001) face.*

(b) *Ex Hrand Djvahirdjian S.A., employed for cutting wafers exposing the (100) face.* In order to increase the conductivity, the wafers were heated in H_2 (1 atm) at 700°C for 1 h; the wafers were cooled slowly in a $\text{N}_2 + \text{H}_2$ atmosphere in order to avoid cracking and superficial reoxidation.

Before reduction, the wafers had been polished with SiC600 paper ($\sim 25\ \mu\text{m}$) and with $5\ \mu\text{m}\ \text{Al}_2\text{O}_3$; then treatment with hydrogen was applied. At this stage, some of the wafers with the (001) face exposed were set apart for studying the influence of surface preparation. The final procedure consisted of polishing after H_2 treatment, again with $5\ \mu\text{m}\ \text{Al}_2\text{O}_3$ and then with $0.05\ \mu\text{m}\ \text{Al}_2\text{O}_3$. This final procedure was applied to some of the wafers with the (001)

face exposed and to all wafers exposing the (100) face.

2.2. Construction of Electrodes

A wafer was mounted in a PTFE holder by pressing it against a gold-plated silver disk, by means of a PTFE screw-cap and a Viton O-ring (Fig. 1). The wafer had been rubbed beforehand at its back with In/Ga alloy for ohmic contact. The interfacial area of the electrode was 0.33 cm^2 .

2.3. Construction of the Measuring Cell

The PTFE holder with the electrode was mounted in a double-wall Pyrex cell, together with a 55-cm^2 -area platinum electrode and a saturated calomel electrode (SCE, see Fig. 1).

2.4. Experimental Setup for Coulostatic Pulses

The cell in which the measurements were performed formed part of a setup (Fig. 2) in which a bias voltage could be applied to the semiconductor electrode, and a current pulse could be transmitted to it. The latter was ob-

FIG. 1. The double-wall cell used for coulostatic pulse experiments: 1. platinum wire, 2. threaded cap (material: Sovirel No. 15), 3. silicon rubber cap, 4. cell, 5. perspex cover, 6. calomel reference electrode, 7. platinum counter electrode, 8. threaded cap (material: PTFE), 9. silicon rubber O-ring, 10. TiO_2 single crystal, 11. gold-plated disk, 12. O-ring, 13. crystal holder (material PTFE), 14. PTFE-coated gasket, 15. connection cap (material: Sovirel No. 15), 16. platinum wire, 17. PTFE-coated magnetic stirrer.

FIG. 2. Experimental setup for pulse relaxation: tr: transient recorder (Difa Tr 1010), pg: pulse generator (Hewlett-Packard 214 b), osc: oscilloscope (Philips PM 3233), mc: microcomputer (Apple II), pt: platinum counter electrode, sc: semiconductor electrode, o: operational amplifier (Burr Brown OPA 103 CM).

tained as a voltage pulse from a Hewlett-Packard 214 b pulse generator; the voltage pulse was converted into a current pulse by two $10\text{-k}\Omega$ resistors. Leakage of charge into the polarization circuit is prevented by two $1\text{-M}\Omega$ resistances; leakage of charge back into the pulse generator is prevented by two diodes. The variable resistor R_v is used to equalize the ohmic resistance of the two branches during application of the pulse, in order to avoid overload effects. The bias potential difference between the semiconductor electrode and the Pt counter electrode is compensated, before the data enter the recording unit. Only the overvoltage due to the pulse is transmitted to a three time base Difa tr 1010 transient recorder. In one pulse, 2000 data points were stored; they were displayed on a Philips PM 3233 oscilloscope and transmitted to an Apple Europlus microcomputer. In the latter they were subjected to curve fitting, Laplace transformation, and complex plane analysis (see section 3).

2.5. Experimental Procedure

During the experiments, the cell was placed in a Faraday cage to reduce pickup of the disturbing signals. The experiments were performed in the dark at $25.0 \pm 0.2^\circ\text{C}$ under a nitrogen atmosphere, using analytical-grade

chemicals and twice-distilled water. Before and after each experiment, the potential of the Pt counter electrode was measured with respect to the SCE. The total measuring time was about 33 s.

The amount of charge supplied in a pulse was measured by a calibration circuit in series with the measuring cell, operated by a separate pulse. The calibration circuit was short-circuited during the pulses subject to analysis.

3. ANALYSIS OF THE DATA

3.1. Overvoltage V s Time Curves

Figure 3 shows a typical overvoltage (η) vs time plot. The breaks in this curve correspond with transitions to another time base; a plot against time with one time base would be a smooth curve (noise excepted). The curve is characteristic of an experiment with the 1-M Ω resistor connected in parallel to the cell (as shown in Fig. 2). If this resistor was disconnected, the curve approached a value of about 90% of the original η value, instead of the value $\eta = 0$. Apparently, no significant charge transfer takes place through the phase boundary; and about 90% of the total relaxation signal is due to the solid phase.

3.2. Calculation of the Impedancy

The first 600 points of an $\eta(t)$ curve were sampled every 3 μ s; the next 900 points were sampled every 0.2 ms; and the remaining points were sampled every 80 ms. From these data, the real and imaginary components of the impedance were calculated by (7–10)

FIG. 3. Typical overvoltage vs time plot.

$$z(j\omega) = \frac{\bar{\eta}(j\omega)}{\bar{i}(j\omega)}, \quad [1]$$

where $\bar{\eta}(j\omega)$ and $\bar{i}(j\omega)$ represent the Laplace-transformed overvoltage and current, respectively; ω is the angular frequency; $j = \sqrt{-1}$. If the coulostatic pulse width is sufficiently short compared with the time scale considered, the Laplace transform of the current is simply (7)

$$\begin{aligned} \bar{i}(j\omega) &= \int_0^\infty i(t)\exp(-j\omega t)dt \\ &= \int_0^\infty q\delta(t)\exp(-j\omega t)dt = q, \end{aligned} \quad [2]$$

where $\delta(t)$ is the Dirac δ -function and q is the total amount of charge introduced into the system considered. $\bar{\eta}(j\omega)$ is calculated by describing $\eta(t)$ as a sum of a set of physically acceptable functions of which the Laplace transforms are known:

$$\eta(t) = \sum_{i=1}^m C_i f_i(t). \quad [3]$$

Since the Laplace transformation is a linear operation,

$$\bar{\eta}(j\omega) = \sum_{i=1}^m \bar{C}_i f_i(t_i). \quad [4]$$

We describe $\eta(t)$ as a sum of a number of exponential functions (each corresponding to a relaxation process) and of $\exp(A^2 t) \operatorname{erfc}(A\sqrt{t})$ functions (each corresponding to a diffusion-controlled process) (4, 5, 7, 11–13):

$$\begin{aligned} \eta(t) &= c_1 \exp(A^2 t) \operatorname{erfc}(A\sqrt{t}) + C_2 \exp(-Bt) \\ &\quad + C_3 \exp(-Dt) + C_4 \exp(-Et). \end{aligned} \quad [5]$$

The best values of the parameters before (C_1 – C_4) and within (A – E) of the functions were determined by an iterative procedure based on nonlinear least-squares algorithms (14, 15). The number of functions of each type was determined by the requirement that an additional function of the same type was rejected by the iteration process, as expressed by one of the following alternatives:

(i) The parameter before the function becomes so small that the contribution of the additional function can be neglected; or

(ii) The parameter within the function becomes so large that the additional function decays to zero before the first sample is taken; or

(iii) The parameters within two $\exp(\)$ $\times$ $\text{erfc}(\)$ or two exponential functions become nearly equal and the functions concerned can therefore be combined to one $\exp(\)\text{erfc}(\)$ or one exponential function.

All our experimental curves could be described by one $\exp(\)\text{erfc}(\)$ and three exponential functions, as expressed by Eq. [5]. The time constants of the exponential functions are in all cases about 0.8×10^{-3} , 0.5, and 6 s. Only that with time constant ≈ 6 s is dependent on the presence or absence of the polarization circuit (see section 3.1). The relaxation functions with time constants of 0.5 and 6 s are independent of the concentration and type of supporting electrolyte and thus are ascribed to the solid state (see section 3.3.).

In the calculation of the impedance as a function of ω , the range of angular frequencies is limited to the range $1/t_{\max} \leq \omega \leq 1/t_{\min}$, with $t_{\max}$ = the total duration of an experiment and $t_{\min}$ = that time after the start of the relaxation, during which overload effects in the amplifier exist.

3.3. Equivalent Circuit Analysis

Thirty-one impedance data points, distributed in the range from 0.01 to 10^4 Hz, were subjected to the complex nonlinear least-squares impedance analysis (16, 17). The circuits described by Abe *et al.* (18), 't Lam *et al.* (19, 20), and Tomkiewicz (21) cannot reproduce our data; our impedance fits are substantially improved by using the equivalent circuit represented in Fig. 4.

Figure 5 shows one example (0.01 M KCl, pH 3.6, bias = 1.67 V vs SCE). The equivalent circuit (Fig. 4b) consists of a Voigt circuit on the semiconductor side and an electrolyte part.

FIG. 4. Equivalent circuits. (a) Circuit as seen in the fitting procedure. Some typical values are shown. (b) Aperiodic equivalent circuit used to fit the impedance data. Complex least-squares estimates and standard deviations are shown for the particular example shown in Fig. 4a (K in Ω s $^{-1/2}$). (c) Maxwell circuit with the same frequency characteristics as the Voigt circuit on the left of Fig. 4b.

The latter is, apart from the leak resistor R_L across the adsorption capacitance C_A , the aperiodic equivalent circuit for adsorption of electroinactive species with a slow adsorption step and negligible charge transfer, as deduced theoretically by Pilla (22). The Voigt circuit on the semiconductor side can be turned into a Maxwell circuit (23), in accordance with the equivalent circuit as proposed by Tomkiewicz (21) for the semiconductor.

The Maxwell circuit represents the solid phase and consists of a semiconductor capacitance C_{sc} in parallel with the capacitance C_{ss} due to surface states.

The time constant of the semiconductor space charge is related to the resistor in the polarization circuit (see section 3.1.). This resistor should be drawn in parallel with the equivalent circuit; however, because the resistance in the solid is much larger than that in the liquid phase, the polarization circuit resistor can be combined in parallel with the semiconductor space charge resistor R_{sc} . The fact that we find 2 M Ω for the apparent semiconductor resistance implies that the space charge resistance itself is ≥ 2 M Ω .

FIG. 5. Complex plane impedance plot. (a) Total impedance, 10^{-2} – 10^4 Hz. (b) High frequency part of (a). (c) Total impedance with the contribution of the semiconductor space charge subtracted. (d) Contribution of the $\exp(-) \operatorname{erfc}(-)$ and the exponential function with time constant $\tau = 0.8$ ms to the total impedance. $\circ$: Data used in the fitting procedure. Δ : Fit to equivalent circuit.

4. RESULTS

4.1. (001) Face

Among the elements of the equivalent circuit, one capacitance (C_{sc} in Fig. 4c) shows a Mott-Schottky-type dependence on the bias (24–26): C_{sc}^{-2} is a linear function of the applied voltage (Fig. 6). In this figure, the agreement between the time fit of the overvoltage data and the equivalent circuit presented in Fig. 4c is illustrated by the coincidence of the two types of data. Thus, C_{sc} can be identified with the space charge capacitance in the solid.

Another element of the equivalent circuit, C_{ss} , shows a dependence on the applied voltage

as expected for surface states (Fig. 7); we therefore identify C_{ss} in Fig. 4c with the surface state capacity.

In order to check whether description of the transport process near the interface by an $\exp(-) \operatorname{erfc}(-)$ function is the best one, we replaced this function by that corresponding with a constant phase-angle impedance:

$$Z_{CPA} = K_{CPA}(j\omega)^{-\alpha} \quad [6]$$

with α variable. The best-fit values of α varied between 0.494 ± 0.003 and 0.518 ± 0.003 for all experiments. This strongly supports our description of this process as a diffusion process because the latter can be described by a

FIG. 6. Mott-Schottky plot in $10^{-2} M$ KCl at pH 3.6. (□) From time fit without intervention of equivalent circuit analysis. (●) From the equivalent circuit shown in Fig. 4.

FIG. 8. Influence of concentration and type of electrolyte on the semiconductor capacitance C_{sc} . C_{sc} obtained from equivalent circuit.

CPA impedance with $\alpha = 0.5$. However, the possibility that the value of α is determined by morphological contributions cannot be strictly ruled out. Z_{CPA} has the characteristics of a Warburg impedance without strictly speaking being one since there is no detectable charge transfer across the TiO_2 /electrolyte solution interface during our experiments.

In $0.1 M$ KCl and in $0.01 M$ KCl at pH 8.6 and 10.9, the parameter R_V in Fig. 4 was too small to be determined. In those cases R_V was omitted from the equivalent circuit.

In Figs. 8 and 9, the Mott-Schottky plot for C_{sc} is shown in various solutions; the pH of all those solutions was about 3.5. It is seen

that C_{sc} is independent of type and concentration of the electrolyte in the solution. This confirms our identification of C_{sc} with a capacitance within the semiconductor; the results agree with those reported by Wilson and Park (27).

The capacitance Z_{CPA} , on the other hand, does depend on the concentration of supporting electrolyte (Fig. 10). The transport process described by this function therefore is a diffusion process ($\alpha = 0.5$) in the liquid. Less

FIG. 7. Capacitance ascribed to surface states as a function of bias ($10^{-2} M$ KCl, pH 3.6).

FIG. 9. Same as Fig. 8; C_{sc} obtained directly from the time fit.

FIG. 10. The parameter K_{CPA} as a function of bias. (○) 10^{-2} M KCl, pH 3.6 and (●) 10^{-1} M KCl, pH 3.2.

pronounced is the dependence of C_A on electrolyte concentration (Fig. 11) and type of electrolyte (Fig. 12). The capacitance C_s depends only slightly on electrolyte concentration (Fig. 13); neither does it strongly depend on the type of electrolyte (Fig. 14). There is a general trend of both C_A and C_s to decrease with increasingly positive bias. Both effects can be explained by a decrease in ϵ_r , the local dielectric constant, with increasing bias.

Although there is no influence of type and concentration of the supporting electrolyte on C_{sc} , the pH does influence this parameter (Fig. 15): a change in pH effects a shift of the C_{sc}^{-2} vs V line toward more negative values. Simultaneously, C_{sc} and C_A change (cf. Figs. 16 and 17, respectively).

FIG. 11. Adsorption capacitance (C_A) as a function of bias. (○) 10^{-2} M KCl, pH 3.6 and (●) 10^{-1} M KCl, pH 3.2.

FIG. 12. Adsorption capacitance as a function of bias for various types of electrolyte. (□) 10^{-2} M KCl, (●) 10^{-2} M KNO_3 , and (○) 10^{-2} M KI.

4.2. (100) Face

Our experimental data for the (100) face could be represented by the same equivalent circuit as that for the data for the (001) face (see Fig. 4), with resistor R_V omitted. Thus, again a shift of the C_{sc}^{-2} vs V line toward more negative values with increasing pH is found (Fig. 18); as in the case of the (001) face, for the (100) face no influence of changes in KCl concentration is found (Fig. 19). However, different curves are observed if the type of the electrolyte is changed.

5. DISCUSSION

5.1. Interpretation of C_{sc}

According to Mott (24) and Schottky (25, 26),

$$C_{sc}^{-2} = 2kT(-1 - \gamma_0)/(N_D e^2 \epsilon_0 \epsilon_r) \quad [7]$$

FIG. 13. Stern capacitance (C_s) as a function of bias. (●) 10^{-2} M KCl and (○) 10^{-1} M KCl.

FIG. 14. Stern capacitance as a function of bias for various types of electrolyte. ($\square$) 10^{-2} M KCl, ($\circ$) 10^{-2} M KNO_3 , and ($\bullet$) 10^{-2} M KI.

where e_0 = the absolute value of the charge of an electron, N_D = the donor concentration, $y_0 = e_0\psi_0/kT$, ψ_0 = the band bending, ϵ_0 = the permittivity of vacuum; and ϵ_r = the relative dielectric constant. Equation [7] is valid under the following conditions:

- $y_0 < 0$,
- $|y_0| \gg 1$,
- in the bulk semiconductor, the donors are completely dissociated.

A linear relation between C_{sc}^{-2} and y_0 indicates that these conditions are fulfilled. The slope of the straight line obtained can be em-

FIG. 15. Influence of pH on the Mott-Schottky behavior in 10^{-2} M KCl; (001) face.

FIG. 16. Stern capacitance as a function of bias in 10^{-2} M KCl. ($\square$) pH 3.6, ($\circ$) pH 8.6, and ($\bullet$) pH 10.9.

ployed to calculate N_D , and from its intercept with the y_0 axis, the flat band potential can be obtained.

When applying Eq. [7] to the data obtained in the present investigation, it should be kept in mind that y_0 is not measured directly. What is known is the total cell potential V ; and changes in V correspond only with changes in ψ_0 , if changes in the other potential drops in the cell can with confidence be neglected. In this respect, especially the potential drop over the Helmholtz layer is subject to uncertainty.

In the present case, the following considerations give us confidence that changes in the total cell potential can be equated with changes in band bending without great error:

(i) At least 90% of the total voltage drop in the cell occurs in the semiconductor (see section 3.1).

(ii) Equating ΔV with $\Delta\psi_0$ leads to linear C_{sc}^{-2} vs y_0 plots (Fig. 6). If changes in the po-

FIG. 17. Adsorption capacitance in 10^{-2} M KCl, as a function of bias for various pH values. Symbols as in Fig. 16.

FIG. 18. Influence of pH on the Mott-Schottky behavior in 10^{-2} M KCl; (100) face.

tential drop over the Helmholtz layer would contribute significantly to ΔV , the agreement with the Mott-Schottky relation (7) would be fortuitous unless there would be a special type of relation between $\Delta\psi_H$ and $\Delta\psi_0$ (e.g., $\Delta\psi_H/\Delta\psi_0$ independent of the bias).

(iii) Equating ΔV with $\Delta\psi_0$ leads, on extrapolation of the C_{sc}^{-2} vs y_0 plots to $C_{sc}^{-2} \rightarrow 0$, to flat band potential values which are independent of the electrolyte concentration (Fig. 8). If the Helmholtz layer potential drop would contribute significantly to changes in the total cell potential, a dependence of electrolyte concentration is expected since the Helmholtz layer capacitance is known to depend on electrolyte concentration.

(iv) The flat band potential values found on the basis of the assumption that changes in other potential drops can be neglected agree with values reported by other investigators (19, 21, 28).

(v) Equating ΔV with $\Delta\psi_0$ leads to N_D values that are reasonable in view of the fact that they lead to values of charges per unit surface area which can be compensated.

The total surface charge in the space charge layer in the semiconductor, per unit interfacial area, can be calculated from

$$q_{sc} = \epsilon_0 \epsilon_r kT (dy/dx)_{x=0} / e_0 \quad [8]$$

with

$$(dy/dx)_{x=0} = \{ (2N_D e_0^2) / (\epsilon_0 \epsilon_r kT) \}^{1/2} \times [\gamma(\exp(y_0) - 1) + \ln((1 + K \exp(-y_0)) / (1 + K))]^{1/2}. \quad [9]$$

Here, $\gamma = N_D^+ / N_D$ in the bulk semiconductor, N_D^+ = the number of dissociated donors per unit volume, $K = \exp((E_D - E_F) / (kT))$, E_D = the donor level in the bulk semiconductors, and E_F = the Fermi level.

For $|E_D - E_F| \gg kT$, $\gamma \simeq 1$, $y_0 < 0$, and $|y_0| \gg 1$ we obtain

$$q_{sc} = (2N_D \epsilon_0 \epsilon_r kT)^{1/2} \times (-1 - y_0)^{1/2}. \quad [10]$$

The Mott-Schottky plots obtained were linear up to y_0 values of about 80. With $N_D = 10.26 \text{ m}^{-3}$ we obtain $q_{sc} = 0.32 \text{ C m}^{-2}$, equivalent to two elementary charges per square nanometer. It has been found (1, 2) that TiO_2 reduced with H_2 has about nine surface hydroxyl groups per square nanometer; though this value was obtained on powdered TiO_2 , we will use it here as a first approximation for single crystal data. The charges in the semiconductor, under the conditions of $y_0 \simeq 80$, are positive; and two charges per square nanometer surface area can easily be compensated, even if all charges in the diffuse double layer, in the Helmholtz layer, and in surface states are negligibly small, by dissociation of surface hydroxyl groups forming TiO^- .

It could be noted that such a high proportion of dissociated TiOH groups at pH 3.6 is at variance with the PZC (pH 6.7 for the powdered TiO_2). However, this PZC was observed on TiO_2 to which no bias was applied. The application of a positive bias corresponding with a pH shift of several units (if the Nernst equation is thought to be valid) will strongly promote dissociation of surface hydroxyl groups.

FIG. 19. Influence of concentration and type of electrolyte on the Mott-Schottky behavior; (100) face.

One objection against the data presented in Table I could be the shift of V_{fb} with increasing pH to more negative bias values. This was observed both for the (100) and for the (001) faces. Qualitatively, it can be explained as being due to increasing dissociation of surface TiOH groups. However, in quantitative respect this shift is, for the (001) face, much more pronounced than would be expected, e.g., from the Nernst equation. At present no solution of this point can be given.

5.2. The Impedance Element

The impedance element in the equivalent circuit (Z_{CPA}), is generally ascribed to a transport process. In our case it was found to depend on the concentration of the supporting electrolyte (Fig. 10) but not on the pH. This may come as a surprise at first sight. However, transport of H^+ ions may be too rapid to be detected by the experimental technique employed. Thus, all transport and charging processes finding expression in the experiments reported here refer to electroinactive species.

Thus the Faradaic current can be neglected with regard to the interfacial charging current. For these conditions, the surface excess of the electroinactive species is given, according to Pilla (22), by

$$\Gamma_0 = K_{CPA} \cdot C_A \cdot \sqrt{D_0} \cdot c_0 \quad [11]$$

with Γ_0 = the surface excess of the electroinactive species, C_A = the adsorption capacity, D_0 = the bulk diffusion coefficient of the electroinactive species, and c_0 = the bulk concentration of the electroinactive species.

TABLE I

Values of N_D (m^{-3}) and V_{fb} (V vs SCE) for TiO_2 in 0.01 M KCl

Face	pH	N_D	V_{fb}
(100)	3.7	4.1×10^{24}	-0.48
	10.6	4.3×10^{24}	-1.13
(001)	3.6	1.1×10^{26}	-0.49
	10.9	1.0×10^{26}	-0.83

FIG. 20. Surface excess of electroinactive species, as calculated by the Pilla equation, as a function of bias; (001) face. (●) 10^{-2} M KCl, (□) 10^{-2} M KNO_3 , and (○) 10^{-2} M KI.

If we apply this formula to our data, we find acceptable values for Γ_0 in 0.01 M solution, of the order of one monolayer, independent of bias and type of the electrolyte (Fig. 20). The latter agrees with data reported by Kazarinov *et al.* (29). As may be seen from the figure, the data are subject to considerable uncertainty. Such a monolayer coverage, independent of bias, can be interpreted as a sign of strong chemisorption of the anions concerned. At low bias values, when there is hardly any charge present in the solid space charge layer, the charge of the chemisorbed anions must be compensated (apart from a small amount of charge which may be present in the Gouy layer and in surface states) by cations near the solid. Increasing bias values introduce positive charges into the space charge layer in the solid. This additional charge must be compensated (again apart from changes in the surface state and Gouy layers charges) by the simultaneous desorption of cations.

This explanation, however, must be regarded with caution: in 0.1 M KCl solution we found by this method Γ_0 values considerably in excess of a monolayer. Apparently, under these conditions, the assumptions in which Eq. [11] was derived are not valid. We mention that ad- and desorption kinetics are consistent with a Langmuir adsorption isotherm and transport of the species to the solid is by diffusion as a rate-determining step. The lack of validity of these assumptions in 0.1 M solution casts doubt on the validity of the Pilla equation at lower electrolyte concentration.

5.3. Differences between the (100) and the (001) Faces

The most pronounced difference between the (100) and the (001) faces found in the present investigation is that in the former case the C_{sc}^{-2} vs bias graph depends on the type of supporting electrolyte (Fig. 19), whereas for the (001) face no effect is found (Figs. 8 and 9). The following is a possible explanation agreeing with the direction of the shift of the Mott-Schottky graph for the (100) face, effected by transition from KNO_3 or KI to KCl as supporting electrolyte. In the (100) face of rutile, there are openings between the oxygen ions, which Cl^- might be able to penetrate and thus be adsorbed on Ti ions. The larger NO_3^- and I^- ions, not being able to penetrate between the oxygen ions, are refined to chemisorption on the latter.

This explanation is to be regarded as hypothetical for the time being because even with a single crystal the interface will not show a structure identical to that of an ideal bulk crystal.

5.4. Relaxation Times Vs Coagulation Times

A certain difference of opinion exists among colloid chemists as to whether processes occurring near an interface during coagulation are rapid enough to permit the use of a stability theory derived on the basis of maintenance of equilibrium (30) between surface potential and surface charge.

Overbeek (31) estimated the collision time to be between 10^{-4} and 10^{-5} s; however, hydrodynamic interaction and electrostatic repulsion during approach (32, 33) may lead to longer collision times.

In the present investigation, for TiO_2 relaxation times have been found which lead to the following statements:

(a) Processes occurring on the liquid side of the interface are fast with regard to collisions.

(b) Adjustment of charges in surface states and in the solid state space charge is slow with regard to collisions.

Thus, the surface charges usually considered in colloid chemistry ($TiO^{(-)}$ and $TiOH_2^{(+)}$, counterions in the inner Helmholtz layer) will be in equilibrium during a collision; the relaxation times corresponding to these processes are too short to lead to nonequilibrium situations.

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