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Specific adsorption of anions on a copper (100) single crystal electrode studied by charge displacement by CO adsorption and infrared spectroscopy

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Abstract

Specific adsorption of anions on a Cu(100) electrode was studied with 0.2 mol/dm³ solutions at 0 °C by voltammetric and FTIR spectroscopic techniques. Voltammetric redox waves of specific adsorption of sulfate and phosphate anions at pH 3 on the Cu(100) electrode are separated from hydrogen evolution reaction (*her*) and is clearly shown by the charge displacement adsorption of CO. Perchlorate anion is not specifically adsorbed on the Cu(100) electrode, and no redox wave is observed. Specific adsorption of phosphate anions on the Cu(100) was studied in more detail in pH ranging from 1.5 to 12.9. The redox potential of the charge displacement CO adsorption–desorption depends on pH with the slope of ca. 30 mV/pH. Under the assumption of electrochemical equilibrium, PO₄³⁻ and/or HPO₄²⁻ are concluded as the adsorbed phosphate species on the Cu(100) electrode in the pH range studied. Most of the negative charge of the phosphate anions is withdrawn by the electrode, bringing the pK_a value of the anions significantly down in the specific adsorption process. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Copper electrode; Anion; Adsorption; Single crystal; pK_a

1. Introduction

Specifically adsorbed anions stay on the electrode surface below the potential of zero charge (*pzc*), and are desorbed from the surface at more negative potential. The adsorption–desorption of anions takes place on Pt at a much more positive potential than the hydrogen evolution reaction (*her*), and the behavior of the specifically adsorbed anions on the Pt electrode has been studied extensively. However, it is not easy to measure the specific adsorption of anion on the electrodes like Cu which have low *pzc*, as *her* can take place at the potential range near the adsorption of anions.

We have discussed earlier that the phosphate anions, specifically adsorbed on the Cu electrode, are displaced by the CO adsorption accompanied with redox voltammetric peaks [1,2]. Conway et al. first reported the charge displacement process during the adsorption of thiourea or dimethylsulfide with platinum electrodes [3]. Clavilier and his coworkers showed that CO adsorption displaces the adsorbed hydrogen or the specifically adsorbed anions from the Pt electrode, giving anodic or cathodic current, respectively [4–6]. The charge displacement process of CO on the copper electrode can be observed by the voltammetric technique, giving *reversible* redox peaks, as CO is *reversibly* adsorbed on the copper electrode surface.

On a Cu(100) electrode, *her* proceeds at -0.65 V versus the standard hydrogen electrode (*she*) in a phos-

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phate electrolyte solution (pH 6.8), and the desorption of specifically adsorbed anions is not observed by the voltammetric technique under argon atmosphere. In CO saturated electrolyte solutions, CO adsorption displaces anion which is subsequently desorbed from the surface at more positive potential than in an argon-saturated solution, giving rise to voltammetric cathodic peaks. During this process, adsorbed CO strongly suppresses *her*. Thus, the specific adsorption–desorption of anions appears to be clearly separated from the *her* current.

The present article presents the adsorption–desorption behavior of some specifically adsorbed anions on a Cu(100) electrode, mainly phosphate, on the basis of voltammetric as well as infrared (IR) spectroscopic measurements. We also propose the determination of adsorbed species by thermodynamic consideration. The pK_a value of the adsorbed phosphate drops significantly owing to the specific adsorption process.

2. Experimental

A copper single crystal Cu(100) (10 mm diameter) was prepared from 99.999% copper metal by the Bridgeman method using a graphite crucible. The crystal orientation was determined by X-ray Laue back reflection method within 0.5° . The surface of the electrode was polished mechanically with diamond slurry down to $0.125\ \mu\text{m}$, and electropolished further in a mixture of concentrated phosphoric acid and sulfuric acid to a mirror finish [7]. Rinsed with ultra pure water, the electrode surface was protected by a drop of slightly acidic ($0.1\ \text{mM}\ \text{HClO}_4$) ultra pure water when transferred to the electrolysis cell.

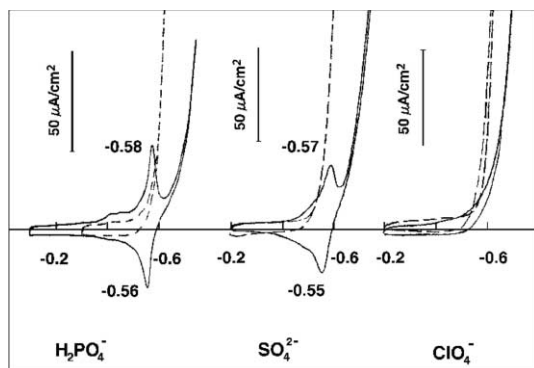


Fig. 1. Cyclic voltammograms of a Cu(100) electrode in $0.2\ \text{mol/dm}^3$ phosphate, sulfate, perchlorate solutions at pH 3 saturated either with argon (broken line) or CO (solid line). Note the potential axis directs negatively. The scanning rate $50\ \text{mV/s}$.

The phosphate solutions of various pH were prepared from the reagent grade of H_3PO_4 , KH_2PO_4 , K_2HPO_4 , and K_3PO_4 . The electrolyte solutions were purified by preelectrolysis using a Pt black cathode overnight. The voltammetric measurements were carried out at $0\ ^\circ\text{C}$. Henceforth the electrode potential is given with reference to *she*, whereas the potential was experimentally measured with respect to an Ag/AgCl reference electrode. For other experimental details one may refer to our earlier publications.

3. Results and discussion

3.1. Charge displacement adsorption process in various electrolyte solutions

Fig. 1 shows the result of the voltammetric measurements of the Cu(100) obtained in pH 3 electrolytes with the total electrolyte concentration $0.2\ \text{mol/dm}^3$ of phosphate, sulfate and perchlorate. The cathodic current of *her* shifts negatively in all the three electrolytes saturated with CO, as *her* is suppressed by the adsorbed CO. Phosphate and sulfate anions give the charge displacement reversible voltammetric peaks in CO saturated electrolytes. IR spectroscopic measurements demonstrated charge displacement process of adsorption–desorption of phosphate and CO on a Cu(100) in a phosphate electrolyte at pH 6.8, published earlier by the present authors [2].

Perchlorate does not give voltammetric peaks in the CO saturated electrolyte (Fig. 1). Perchlorate anions are not specifically adsorbed on the electrode, but are still attracted to the electrode by the Coulombic force above the *pzc*, $-0.54\ \text{V}$ for Cu(100) [8], in the absence of CO. CO, weakly adsorbed on the electrode, will displace the perchlorate anions at the potential more positive than *pzc*. Fig. 2 shows the results of in situ IR spectroscopic measurements in the perchlorate electrolyte. The IR absorption at ca. $2060\ \text{cm}^{-1}$ of C–O stretching is observed at $-0.25\ \text{V}$. The IR absorption increases with an increase in the negative potential, showing the progress of CO adsorption on the electrode surface. The charge displacement redox peaks are not observed during the adsorption–desorption of perchlorate in Fig. 1, and this fact confirms that perchlorate is not specifically adsorbed on the electrode.

3.2. Voltammetric measurements of Cu(100) in various phosphate solutions

Fig. 3 shows voltammograms of the Cu(100) in various phosphate electrolyte solutions of pH 1.5–12.9 in a constant total phosphate concentration of $0.2\ \text{mol/dm}^3$ saturated either with argon or CO. In argon-saturated solutions, no redox peak appears in the solutions of pH

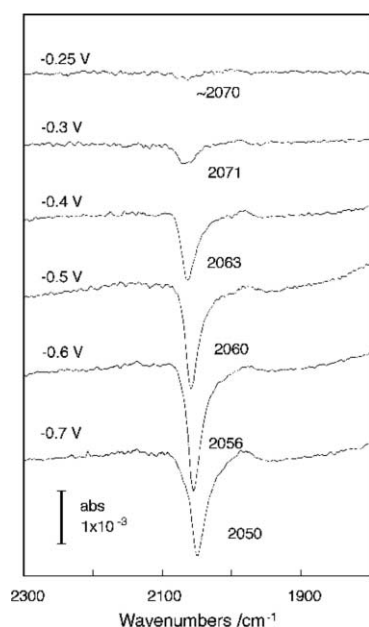


Fig. 2. In situ IR spectra obtained from the Cu(100) electrode in 0.2 mol/dm³ perchlorate solution at pH 3 saturated with CO at various electrode potentials with the reference potential – 0.2 V vs. *she*.

1.5–7.8. Cathodic peaks of anion desorption are observed in argon-saturated solutions from pH 8.8 to 12.9, separated from *her*. The redox voltammetric peaks of charge displacement process appear in the CO-saturated solutions in the entire pH range.

Fig. 4 demonstrates that the potential of the charge displacement redox peaks depends linearly on the pH of the phosphate electrolytes. The potentials obtained from the cathodic scanning differ from the anodic ones, and the two correlation straight lines are given in Fig. 4. The slopes of the two straight lines are – 24 and – 31 mV/pH. Aramata et al. reported the specific ad-

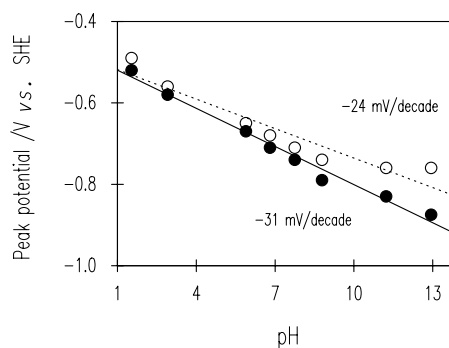
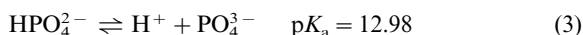
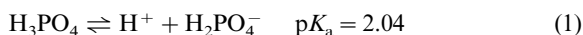


Fig. 4. Potentials of the charge displacement redox peaks correlated with pH of the solutions. Slopes of the straight lines are given for the anodic (dotted line) and cathodic (solid line) scanings.

sorption of phosphate anion on Pt(111) by voltammetric measurement [9]. They obtained the pH dependence of the anion adsorption to be – 52 mV/pH in the region of pH < 2.1, and – 40 mV/pH in the solution of 2.1 < pH < 7.2.

In aqueous solutions containing phosphate anions, acid–base equilibria hold as shown below with pK_a values at 0 °C calculated from the value at 25 °C [10] and the temperature coefficient [11].



The prevalent phosphate species among H_3PO_4 , H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} varies in accordance with the pH of the solution. It is interesting that a single straight line can correlate the peak potential with the pH values (Fig. 4).

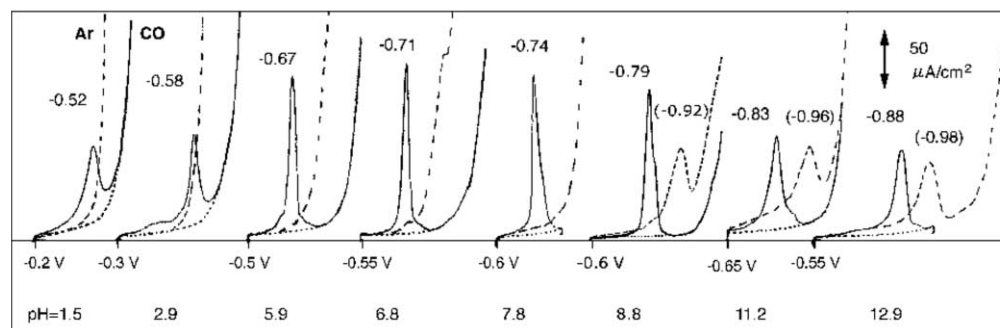
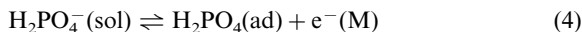


Fig. 3. Cathodic voltammograms of the Cu(100) electrode in 0.2 mol/dm³ phosphate solutions at various pH saturated either with argon (broken line) or CO (solid line). The scanning rate 50 mV/s. The charge displacement cathodic peaks of phosphate desorption appear in CO-saturated solutions with the potentials indicated at the top of the peaks in V vs. *she*. The baselines for calculating the electricity of the peak are indicated in dotted lines.

3.3. Adsorption equilibria of phosphate anions between the electrolyte solutions and the electrode

With regard to the specific adsorption of H_2PO_4^- , the electrochemical equilibrium will hold between the electrode surface and the solutions at an electrode potential, in addition to the acid–base equilibria of phosphate anions in an aqueous solution as mentioned above.



where (sol) denotes species in the solution, (ad) the adsorbed species, and (M) the metal electrode. The electrochemical potential on both sides of the reaction mentioned above must be equal to each other.

$$\begin{aligned} \mu[\text{H}_2\text{PO}_4^-(\text{sol})] - F\phi_{(\text{sol})} \\ = \mu[\text{H}_2\text{PO}_4(\text{ad})] + \mu[\text{e}^-(\text{M})] - F\phi(\text{M}) \end{aligned} \quad (5)$$

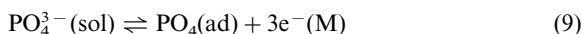
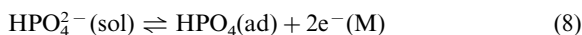
where μ denotes the chemical potential, F the Faraday constant, and ϕ the electric potential. We define the chemical potentials at the standard state, μ_0 , of the adsorbates as those at the coverage of 50%. The chemical potential of the solute is as given below

$$\mu = \mu_0(i) + RT \ln a[i(\text{sol})] \quad (6)$$

where a denotes the activity, and the other letters have the usual meanings. Hence, the electrode potential given for the standard state of adsorption is

$$\begin{aligned} \phi(\text{M}) - \phi(\text{sol}) = (1/F) \\ \{ \mu_0[\text{H}_2\text{PO}_4(\text{ad})] - \mu_0[\text{H}_2\text{PO}_4^-(\text{sol})] \\ + \mu[\text{e}^-(\text{M})] \} \\ - (RT/F) \ln a[\text{H}_2\text{PO}_4^-(\text{sol})] \end{aligned} \quad (7)$$

The other two anions, HPO_4^{2-} and PO_4^{3-} , will have similar relationships as given below



Regarding the electrochemical potential, we obtain the following relations for the two anions, respectively,

$$\begin{aligned} \mu[\text{HPO}_4^{2-}(\text{sol})] - 2F\phi(\text{sol}) \\ = \mu[\text{HPO}_4(\text{ad})] + 2\mu[\text{e}^-(\text{M})] - 2F\phi(\text{M}) \end{aligned} \quad (10)$$

$$\begin{aligned} \mu[\text{PO}_4^{3-}(\text{sol})] - 3F\phi(\text{sol}) \\ = \mu[\text{PO}_4(\text{ad})] + 3\mu[\text{e}^-(\text{M})] - 3F\phi(\text{M}) \end{aligned} \quad (11)$$

Hence, the electrode potentials for the standard state of adsorption are given as

$$\begin{aligned} \Phi(\text{M}) - \Phi(\text{sol}) = (1/2F) \\ \{ \mu_0[\text{HPO}_4(\text{ad})] - \mu_0[\text{HPO}_4^{2-}(\text{sol})] \\ + 2\mu[\text{e}^-(\text{M})] \} \\ - (RT/2F) \ln a[\text{HPO}_4^{2-}(\text{sol})] \end{aligned} \quad (12)$$

$$\Phi(\text{M}) - \Phi(\text{sol}) = (1/3F)$$

$$\begin{aligned} \{ \mu_0[\text{PO}_4(\text{ad})] - \mu_0[\text{PO}_4^{3-}(\text{sol})] \\ + 3\mu[\text{e}^-(\text{M})] \} - (RT/3F) \\ \ln a[\text{PO}_4^{3-}(\text{sol})] \end{aligned} \quad (13)$$

Dissociative adsorption, such as

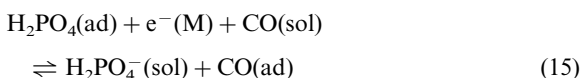


may take place as an actual process[12]. If reaction (14) is in equilibrium, then equilibrium (14) is equivalent to the sum of the two equilibria (3) and (9). As equilibrium (3) holds in the aqueous phosphate solutions, the discussion of equilibrium (14) is equivalent to that of equilibrium (9) in the thermodynamic sense.

3.4. Equilibria of charge displacement adsorption

The formulation mentioned above is applied to the charge displacement by CO adsorption, as discussed for the three adsorbed species below.

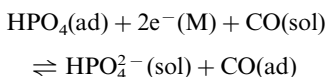
3.4.1. Adsorption of H_2PO_4



The electrode potential is given with the temperature at 0 °C and the values for the constants are inserted as given below

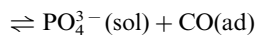
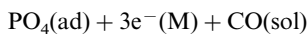
$$\begin{aligned} \Phi(\text{M}) - \Phi(\text{sol}) = (1/F) \\ \{ \mu_0[\text{H}_2\text{PO}_4(\text{ad})] - \mu_0[\text{HPO}_4^-(\text{sol})] \\ + \mu[\text{e}^-(\text{M})] + \mu[\text{CO}(\text{sol})] \\ - \mu_0[\text{CO}(\text{ad})] \} \\ - (RT/F) \ln a[\text{H}_2\text{PO}_4^-(\text{sol})] \\ = \text{const.} - (54 \text{ mV}) \log a[\text{H}_2\text{PO}_4^-(\text{sol})] \end{aligned} \quad (16)$$

3.4.2. Adsorption of HPO_4



$$\begin{aligned} \Phi(\text{M}) - \Phi(\text{sol}) = (1/2F) \\ \{ \mu_0[\text{HPO}_4(\text{ad})] - \mu_0[\text{HPO}_4^{2-}(\text{sol})] \\ + 2\mu[\text{e}^-(\text{M})] + \mu[\text{CO}(\text{sol})] \\ - \mu_0[\text{CO}(\text{ad})] \} \\ - (RT/2F) \ln a[\text{HPO}_4^{2-}(\text{sol})] \\ = \text{const.} - (27 \text{ mV}) \log a[\text{HPO}_4^{2-}(\text{sol})] \end{aligned} \quad (17)$$

3.4.3. Adsorption of PO_4



$$\Phi(M) - \Phi(sol) = (1/3F)$$

$$\begin{aligned} & \{\mu_0[PO_4(ad)] - \mu_0[PO_4^{3-}(sol)] \\ & + 3\mu[e^-(M)] + \mu[CO(sol)] \\ & - \mu_0[CO(ad)]\} \\ & - (RT/3F) \ln a[PO_4^{3-}(sol)] \\ & = \text{const.} - (18 \text{ mV}) \log a[PO_4^{3-}(sol)] \end{aligned} \quad (18)$$

3.5. Correlations of the peak potential with the anion activities

If $H_2PO_4(ad)$ is adsorbed on the electrode surface, then the electrode potentials for the standard state of adsorption may be correlated with $\log a[H_2PO_4^-(sol)]$

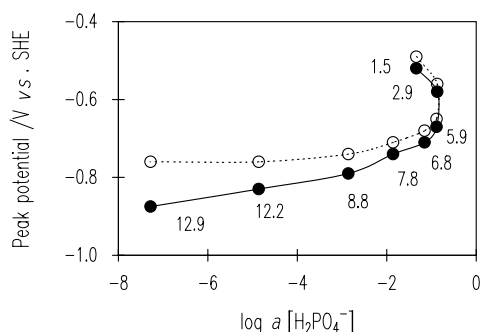


Fig. 5. Potentials of the charge displacement redox peaks correlated with $\log a[H_2PO_4^-]$. Cathodic (solid line) and anodic (dotted line) scanings are shown separately. pH values are given close to the data points.

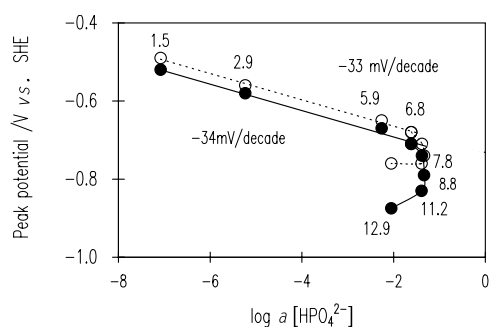


Fig. 6. Potentials of the charge displacement redox peaks correlated with $a[HPO_4^{2-}]$. Cathodic (solid line) and anodic (dotted line) scanings are shown separately with the slopes of the straight part of the correlation lines indicated. pH values are given close to the data points.

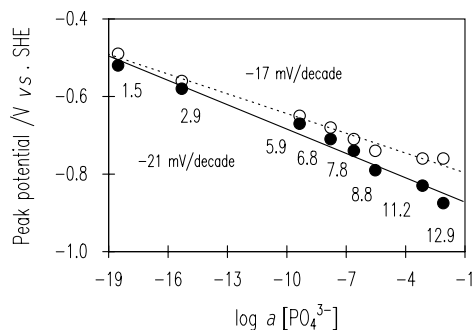


Fig. 7. Potentials of the charge displacement redox peaks correlated with $a[PO_4^{3-}]$. Cathodic (solid line) and anodic (dotted line) scanings are shown separately with the slopes of the straight correlation lines indicated. pH values are given close to the data points.

by a straight line with the slope -54 mV/decade . We tentatively take the peak potential of the redox waves instead of the potential at the standard state. We shall discuss the validity of this choice later.

Fig. 5 shows the relation between the peak potential and the activity of $H_2PO_4^-(sol)$. The activity coefficient of $H_2PO_4^-(sol)$ was calculated according to the Davies equation [11]. Fig. 5 does not give a straight line with the slope -54 mV/decade predicted in Section 3.4.1. Fig. 6, which relate the peak potential and the activity of $HPO_4^{2-}(sol)$, gives straight lines for cathodic and anodic scanning in the pH range between 1.5 and 6.8 with slopes -34 and -33 mV/decade , respectively. Fig. 7 correlates the peak potential and the activity of $PO_4^{3-}(sol)$ by straight lines for cathodic and anodic scanning in the entire pH range between 1.5 and 12.9 with slopes -21 and -17 mV/decade , respectively.

3.6. Validity of the peak potential taken as the potential of the standard state adsorption

The current of the voltammetric peaks were integrated against the potential, and we obtained the electric charges of adsorption that correspond to the coverage. We can thus determine the potentials at 50% coverage. The potential values at 50% coverage obtained from the cathodic scanning deviate slightly from the peak potential toward the positive direction, and the maximum deviation was 20 mV for pH 1.5. We plotted the potential values against $\log[PO_4^{3-}]$ and obtained a straight line with slope of 21 mV . The value of the slope agrees accurately with that obtained from the peak potentials of the cathodic waves shown in Fig. 7. Thus, it is enough to employ the peak potentials of the redox peaks instead of the potential at 50% coverage, as long as the discussion is made with respect to the slope of the straight lines.

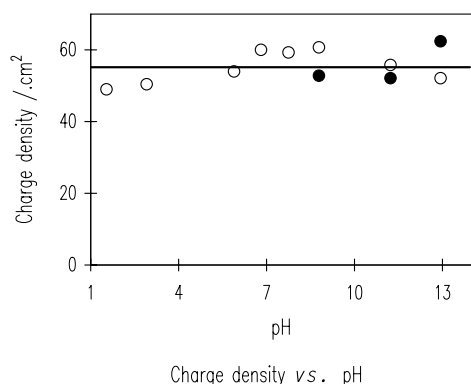


Fig. 8. Electric charge of the redox peaks given as a function of pH of the solutions. The open circles are obtained from CO-saturated solutions and the filled circles from argon-saturated solutions for pH 8.8 to 12.9.

3.7. Adsorbed species on the Cu(100) electrode

Fig. 5 does not give a straight line with the slope of 54 mV/decade, and thus apparently excludes the possibility of the adsorption of $\text{H}_2\text{PO}_4(\text{ad})$ on the electrode.

Fig. 6 shows the linear parts in the correlation lines. The slope of the linear parts are -33 or -34 mV/decade, which could be compatible with -27 mV/decade for the adsorption of HPO_4 as predicted in the formulation mentioned (Section 3.4.2) above, if one takes into consideration the precision of the measurements. Thus, the adsorbed species might possibly be $\text{HPO}_4(\text{ad})$ in this pH range.

The two straight lines are obtained in the whole pH range as shown in Fig. 7; the average slope of the two straight lines is -19 mV/decade, compatible with the formulation given above (Section 3.4.3). In argon-saturated solutions, redox peaks were also obtained in pH 8.8–12.9 as shown in Fig. 3. The correlation between the potential of the redox peaks under argon atmosphere and $\log a[\text{PO}_4^{3-}]$ was tested, giving two straight lines obtained by the anodic and cathodic scanning, respectively. The slope of the straight lines was -23 and -18 mV/decade. These values are consistent with those shown in Fig. 7.

The above-mentioned fact suggests that the adsorbed species may be $\text{PO}_4(\text{ad})$ in a wide pH range. PO_4^{3-} is prevalent in an aqueous solution of pH near or above 12.98 according to the $\text{p}K_a$ value; not prevalent far below pH 12.98. It is interesting that $\text{PO}_4(\text{ad})$ is a possible adsorbed species, whereas the prevalent anion in the solution is HPO_4^{2-} or H_2PO_4^- in the pH range.

3.8. Adsorbed species, $\text{HPO}_4(\text{ad})$ or $\text{PO}_4(\text{ad})$

In accordance with the discussions above, the actually adsorbed species on Cu(100) electrode may be

$\text{PO}_4(\text{ad})$, but we cannot exclude the possibility that $\text{HPO}_4(\text{ad})$ is an adsorbed species as described above. We need to study Fig. 6 in more detail.

In a dissociative adsorption



the electrode potential is given as

$$\begin{aligned} E &= \Phi(\text{M}) - \Phi(\text{sol}) \\ &= \text{const.} + (RT/3F) \ln \left\{ \frac{a[\text{PO}_4(\text{ad})]a[\text{H}^+]}{a[\text{HPO}_4^{2-}(\text{sol})]} \right\} \end{aligned}$$

Taking $a[\text{PO}_4(\text{ad})]$ as unity for the standard state of adsorption, the slope of the correlation line between the potential and $\ln a[\text{HPO}_4^{2-}(\text{sol})]$ is

$$\begin{aligned} &\left(\frac{\partial E}{\partial \ln a[\text{HPO}_4^{2-}]} \right)_{a[\text{PO}_4(\text{ads})]} \\ &= -\frac{RT}{3F} + \frac{RT}{3F} \left(\frac{\partial \ln a[\text{H}^+]}{\partial a[\text{HPO}_4^{2-}]} \right)_{a[\text{PO}_4(\text{ads})]} \end{aligned}$$

One can calculate the composition of phosphate solution under conditions (1)–(3) with the total concentration of 0.2 mol/dm^3 . Thus, the concentration of the species, H_3PO_4 , H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} as a function of pH is obtained. The value of $(\partial \ln a[\text{H}^+]/\partial a[\text{HPO}_4^{2-}])_{a[\text{PO}_4(\text{ads})]}$ is -0.74 for pH between 1.5 and 3.0. The slope of the correlation line is estimated as -31.4 mV/decade.

Fig. 6 provides the correlation between the potential and the $a[\text{HPO}_4^{2-}(\text{sol})]$. If the adsorbed species is HPO_4 , the slope must be -27 mV/decade from formulation in Section 3.4.2; and if $\text{PO}_4(\text{ad})$ is adsorbed, the slope is expected to be -31.4 mV/decade as given above. The experimental value is from -33 to -34 mV/decade, which apparently supports that $\text{PO}_4(\text{ad})$ is the adsorbed species. Fig. 7 gives the correlation between the potential and the $a[\text{PO}_4^{3-}(\text{sol})]$, and the slope of the straight line 19 mV/decade confirms that $\text{PO}_4(\text{ad})$ is the adsorbed species in the whole pH range. Thus, we can conclude that $\text{PO}_4(\text{ad})$ is the probable adsorbed species even in the solutions of low pH.

3.9. Electric charge of the redox peaks at various pH

Fig. 8 shows the electric charges of the redox peaks at various pH obtained from CO-saturated and argon-saturated solutions. The electric charges were determined from Fig. 3 with the dotted lines assumed as the base lines. The data from both solutions agree with each other; this fact confirms that the redox peaks from both solutions are derived from the same process, i.e. desorption of specific adsorbed anions. The data scatter a little as shown in Fig. 8, but the values are approximately constant in the wide pH range. The constancy of the electric charge shown in Fig. 8 apparently confirms that the adsorbed species is $\text{PO}_4(\text{ad})$ in the entire pH

range. However, further discussion calls for more precise measurements.

3.10. IR spectroscopic measurements of adsorbed phosphate anion

In situ IR spectroscopic measurements of the electrode surface in pHs 6.8 and 11.2 gave spectra presented in Fig. 9. The two spectra show the identical feature of the IR absorption around 1100 cm^{-1} assigned as the stretching of P–O bond in PO_4 within the IR resolution limit of 4 cm^{-1} , confirming that the species in the two pH solutions are identical. In this pH range, the adsorbed species are probably $\text{PO}_4(\text{ad})$. The measurements below pH 6 are impossible because of high hydrogen evolution.

3.11. Sorption valence

Sorption valence is defined as

$$\text{Sorption valence} = -\frac{1}{F} \left(\frac{\partial \mu_A}{\partial E} \right)_{\Gamma_{\text{ads}}}$$

where Γ_{ads} denotes the surface excess of the adsorbed anion [13,14]. μ_A , chemical potential of the anion in the solution, is substituted by the following activity

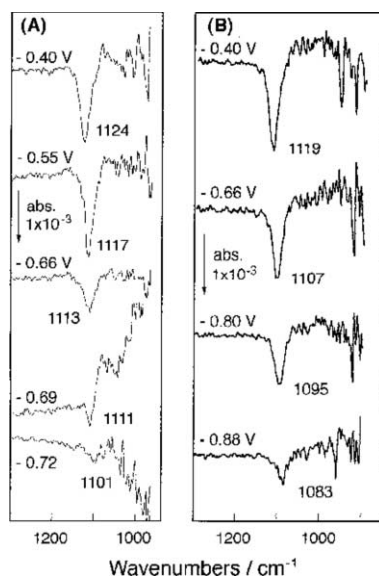


Fig. 9. In situ IR spectra of phosphate anion adsorbed on the Cu(100) electrode in pH 6.8 (A) and 11.2 (B) solutions with the potential indicated. The IR absorption by anions dissolved in the solutions were eliminated using difference of p-polarized and s-polarized spectra. The wavenumbers of the IR absorption bands are given. The reference spectrum was acquired at -0.8 V in the pH 6.8 solution, and -0.95 V in the pH 11.2 solution.

$$\text{Sorption valence} = -\frac{RT}{F} \left(\frac{\partial \ln a_A}{\partial E} \right)_{\Gamma_{\text{ads}}}$$

The sorption valence is obtained readily from the results in Fig. 7, i.e. 3 for $\text{PO}_4(\text{ad})$. These values do not necessarily correspond to the exact number of transferred electrons [15], but still indicate that a considerable amount of the negative charge is withdrawn to the electrode from PO_4^{3-} , forming the covalent bond.

3.12. Lowering of pK_a of the adsorbed species

The adsorbed species, PO_4 , is less acidic than those prevalent in aqueous solution. Other authors have reported similar phenomena. Iwasita et al. observed that carbonate and/or bicarbonate ion is adsorbed on Pt(110) and Pt(111) by IR spectroscopy in CO_2 -saturated 0.1 M HClO_4 where neither the carbonate nor the bicarbonate ion is stable [16–18]. They also reported that sulfate anions are adsorbed on Pt(111) in pH 0.23 K_2SO_4 in the HF–KF base solution where the prevalent anion is HSO_4^- [19]. They suggested changes in the strength of acids at the surface as compared with the solution phase. Osawa et al. reported that sulfate rather than bisulfate is adsorbed on Pt(111) in $0.1\text{ M H}_2\text{SO}_4$ according to their IR spectroscopic study [20]. Fukuda and Aramata presumed that CH_3COO would be the specifically adsorbed species on Pt(111) from a solution of CH_3COOH and HClO_4 of pH 2 [12], in which the stable species in the solution is CH_3COOH , and not CH_3COO^- . These findings obviously indicate that the pK_a values of adsorbed species drop to a significant extent in comparison with those in an aqueous solution.

As is well known, chlorine substituted acetic acids is a good example that the withdrawal of electron to chlorine atoms promotes the release of proton [21]. As the number of the substituted chlorine atoms increases, the pK_a value remarkably decreases; i.e. 4.56 for CH_3COOH , 2.68 for CH_2ClCOOH , 1.30 for CHCl_2COOH , and 0.66 for CCl_3COOH . In a similar manner, the pK_a value of HPO_4^{2-} or PO_4^{3-} will significantly drop by the withdrawal of electrons from anions in the specific adsorption process.

4. Conclusions

1. Voltammetric redox waves of specific adsorption of anions on a Cu(100) electrode was separated from *her* and shown clearly by the charge displacement adsorption of CO.
2. The adsorption of sulfate and phosphate anions is accompanied with redox waves at pH 3, whereas perchlorate anion is not specifically adsorbed on the Cu(100) electrode and no redox wave was observed.

3. The redox potential of the charge displacement process depends on the pH with the slope of ca. 30 mV/pH. Under the assumption of electrochemical equilibrium, PO_4^{3-} is concluded as the adsorbed phosphate species on the Cu(100) electrode in the pH range studied.
4. The negative charge of the anions is partially withdrawn to the electrode, bringing the $\text{p}K_{\text{a}}$ value of the anions significantly down in the specific adsorption process.

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