New electrochromism isotherm in anodic iridium oxide films

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We show that there are two distinct electrochromic processes in anodic iridium oxide films. The measured isotherms for both processes have simple theoretical forms dominated by internal entropy changes of noninteracting particles. Such isotherms have never before been observed for amorphous films.

In spite of its great importance for catalysis, the metal:aqueous-electrolyte interface is very poorly understood.[1] For acidic solutions iridium is the best oxygen catalyst known to date.[2] At the metal:aqueous-electrolyte interface only iridium among the noble metals can form a thick oxide film[3] (up to 5000 Å), referred to as an anodic iridium oxide film or AIROF. This AIROF also has remarkable electrochromic[4-7] properties. Since the electrochromism of AIROF's and that of amorphous WO_3 are somewhat similar[8-10] and since the electrochromism of WO_3 has been explained by proton injection, it is commonly assumed[11,12] that proton injection is necessary for the electrochromism of AIROF's.

In this paper we show for the first time that there are *two* different electrochromic processes in AIROF's. The measured isotherms for both processes have simple theoretical forms dominated by internal entropy changes of noninteracting particles. Such isotherms have never before been observed for amorphous films. We also show from this analysis that neither process is consistent with the simple proton-injection model which prevails[9,10] in WO_3. The forms of the isotherms greatly restrict the classes of electrochromic processes which can explain the properties of AIROF's.

Crandall *et al.*[13,14] have successfully explained the electrochromic mechanism of amorphous WO_3 by a hydrogen-injection model. Electrocoloration occurs when electrons and protons are injected into the WO_3 film forming the tungsten bronze H_xWO_3. Bleaching takes place by space-charge-limited double extraction of electrons and protons. Coloration is due to the reduced W^{5+} ion, and as coloration proceeds, an internal emf arises from the chemical potential of hydrogen in H_xWO_3. The Crandall *et al.* measurements[15,16] of the internal emf E at room temperature for $0.002 \leqslant x \leqslant 0.5$ agree well with the form

$$E = E_0 + bx + k_BT \ln[x/(1-x)]^2, \qquad (1)$$

with $b = 0.53$ eV (k_B is the Boltzmann constant;

T is the absolute temperature). The parameter E_0 depends on the reference electrode and is thus physically irrelevant. The parameter b is a measure of pair interactions, and dominates Eq. (1) at room temperature for $0.1 \leqslant x \leqslant 0.5$. This large pair-interaction term for the proton-electron injection mechanism will be used later to help identify the physical mechanisms dominant in AIROF's. The logarithmic part of Eq. (1) is due to the entropy of mixing H with WO_3. The exponent 2 indicates that the injected electron and proton are uncorrelated. Recent experiments[17] have confirmed this result.

We have measured the internal emf of AIROF's in aqueous solutions over the pH range 0–14 and temperature range 0–75 °C. Although most of the data will be presented in detail elsewhere,[18] briefly we find (i) that AIROF's develop an internal emf E during coloration and have the external properties of thin film batteries; and (ii) that their internal emf is a function only of the charge per unit volume Q. As a consequence of Eq. (1) and since the charging process is sufficiently fast, cyclic voltammograms[19] for AIROF's yield directly dQ/dE vs E, and thus provide the most convenient way to obtain the isotherm $E(Q)$.

We show in Fig. 1 the pH dependences of the maxima in the cyclic voltammograms over the pH range 0–14 at room temperature. The two curves superimposed are anodic scans for pH $= 0.3$ and 14, respectively (the processes are highly reversible and the cathodic scans are almost mirror images about the abscissa). The square points trace the pH dependence of the A peak which dominates the voltammogram in acidic solutions. It can be seen that this peak shifts at a rate of 59 mV/pH unit. At high pH a new peak B appears in the voltammogram. Its dependence upon pH is shown by the round points which also shift at a rate of 59 mV/pH unit. Simultaneous reflectivity measurements to be reported elsewhere[18] show that for pH $= 14$, the electrochromism takes place primarily around B. Thus there are two distinct processes A and B preceeding O_2
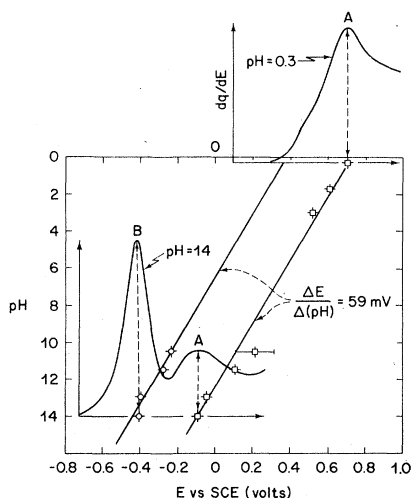
FIG. 1. pH dependence of maxima in cyclic voltammo-
grams for AIROF's at room temperature measured at a
sweep rate of 100 mV/sec. The two solid curves are
anodic scans and measure dq/dE (in arbitrary units) as
a function of the internal emf E (in volts versus a satu-
rated calomel electrode) at pH = 0.3 and pH = 14. The
square (round) points trace the pH dependence of the A
(B) peaks. Both peaks shift at the rate of 59 mV/pH unit
(solid lines).

evolution, both of which produce electrochromism.

The 59 mV/pH unit shift of the peaks does not
help us to discriminate between proton injection
and other models for the electrochemistry of the
AIROF: solution interface. From the Nernst
equation, emf's measured at room temperature
shift by 59 mV/pH unit for any reaction involving
H^+, OH^-, or O_2^- regardless of whether or not such
ions are injected into the electrode.[20] Although
the pH dependence of the maxima is of little value,
we point out in this paper that the *shapes of the
voltammogram peaks* contain a considerable
amount of new physical information.[21] By fitting
these shapes to simple theoretical forms, we
greatly restrict the classes of processes which
can explain the properties of AIROF's.

As we will show in detail elsewhere,[18] the
AIROF's are operationally entropy cells, with

$$\Delta S = k_B \ln[q/(1-q)]^n , \qquad (2)$$

where $q = Q/Q_{max}$ is the normalized charge per
unit volume, ΔS is the entropy change associated
with q, and n, the configurational exponent, is an
integer. It follows from Eq. (2) that the shapes
of the current peaks around the equilibrium value
E_0 are related to the internal emf E by

$$i \propto \frac{dq}{dE} = (4nk_BT)^{-1}\mathrm{cosh}^{-2}[(E-E_0)/2nk_BT] , \qquad (3)$$

where i is the current measured by cyclic voltam-
metry under reversible and diffusionless con-
ditions and absence of other reactions, and we set
the electronic charge e equal to unity. We find
that both the A and B peaks have the form of Eq.
(3) with $n = 3$ and $n = 2$, respectively. For the B
peak, values of dq/dE calculated from Eq. (3),
using a configurational exponent $n = 2$, are com-
pared with experiment in Fig. 2. Although there
are no adjustable parameters (except for the
trivial E_0) and no base line corrections, the
agreement between theory and experiment is ex-
cellent over the entire range $0.02 \leqslant q \leqslant 0.98$.

For the A voltammogram peak in AIROF's, a
similar analysis at pH = 0.3 also leads to an iso-
therm with ΔS having the form of Eq. (2) but with
a configurational exponent $n = 3$. The range of
validity of the fit is $0.07 \leqslant q \leqslant 0.8$. Thus for both
the A and B processes we find pure entropy iso-
therms. This is very unusual since in the colora-
tion of WO_3,[15,16] and often in surface electro-
adsorption,[1] the pair-interaction term in the free
energy is comparable to or larger than the en-
tropy term. To check our results we have tried
to fit the A and B peaks using isotherms of the
form

$$E - E_0 = bq + k_BT \ln[q/(1-q)]^n \qquad (4)$$

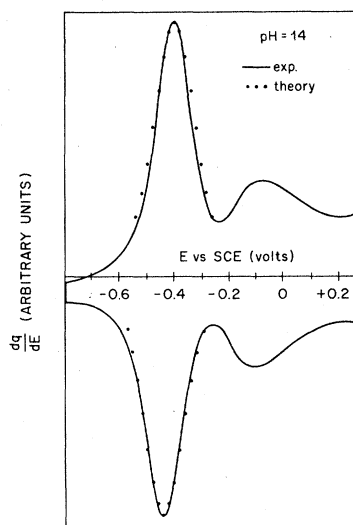with b and n as parameters. The best fit is ob-

FIG. 2. The derivative of the electrochromism iso-
therm of process B (cf. Fig. 1) at pH = 14. The solid
curve was obtained experimentally by cyclic voltam-
metry under reversible conditions and negligible diffusion.
The points are theoretical values from Eq. (3) using a
configurational exponent $n = 2$. No other parameter ent-
ers the theory and no baseline adjustments were made.
For clarity in this figure we show only a few points
rather than a continuous line.

tained for $b = 0$, and $n = 2$ (B peak) or $n = 3$ (A peak). An upper limit on b is 0.01 eV for both A and B. We have independently checked this result by measuring the temperature dependence of the isotherms. This represents the first measurement of the temperature dependence of the internal emf of an electrochromic material. Equations 3 and 4 have an explicit temperature dependence which depends critically upon the value of the configurational exponent n. The temperature dependence of the slope of the A isotherms at $q = 0.5$ is shown in Fig. 3 and compared to theoretical curves for various values of n. It is clear that the experimental data are in good agreement with the value of $n = 3$ determined independently by the fit to the shape of the A peak at room temperature.[18]

For $H_x WO_3$ and the tungsten bronzes in general,[22] the interaction term dominates over the entropy term in the free energy. Since we have shown that the noninteracting model ($b = 0$) describes the A and B processes in AIROF's over unusually large ranges in q, we conclude that the A and B electrochromic processes are *qualitatively different* from the proton injection of WO_3 coloration.

A study[18] of the isothermal "compressibility" $k_T = (1/q)(dE/dq)$ vs q also rules out the possibility that the two electrochromic processes are due to ordering fluctuations around λ-point singularities. Thompson[23] has observed such fluctuations in $Li_x TiS_2$.

Since the two distinct processes cannot both be simple proton injection, our results show clearly that other processes can accomplish coloration in AIROF's. In aqueous solutions the likely physical mechanisms producing electrochromism in AIROF's consistent with a 59 mV/pH unit shift $b = 0$ and two different configurational exponents, involve OH^- adsorption directly or from the splitting of water. Such a model is supported by a detailed study[18] of the A and B peak intensities as a function of pH. Whereas the A peak intensity is approximately constant in the pH range 0–12, indicating adsorption from the splitting of water, the B peak intensity increases rapidly in the pH range 12–14, indicating adsorption of OH^- directly.

AIROF's are highly porous[3] and have a large surface-to-volume ratio, so that bulk and surface effects are not easily distinguished. We note that the AIROF isotherms are perfectly isomorphic to dissociative adsorption isotherms for diatomic
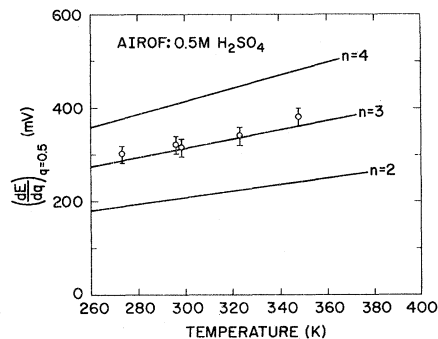

FIG. 3. Temperature dependence of the slope of the A-electrochromism isotherm at $q = 0.5$. The solid lines are theoretical values from Eq. (3) for configurational exponents $n = 4$, 3, and 2, respectively.

and triatomic molecules.[24] Also a strong similarity exists between the B-peak isotherm and the oxygen electrodesorption[25] reaction on Pt. This process has been interpreted[26] in terms of a Langmuir isotherm[1] with repulsive pair interactions. However, a reexamination[18] of published data for Pt shows that the best fit to the data is obtained with a dissociative adsorption isotherm ($n = 2; b = 0$) corresponding, for example, to $Pt^+ OH^- \rightarrow Pt + OH$. An analogous process could take place in AIROF's. If the AIROF electrochromism is in fact a surface controlled process, A and B result in different surface structures following electrocoloration. The markedly different catalytic properties[2] of AIROF's on Ir in pH = 0 and pH = 14 solutions could be due to the differences between the surface structures created by the A and B electrocoloration processes.

In summary, we have observed a new electrochromism isotherm in AIROF's, and shown that there are *two* distinct electrochromic processes with different isotherms. Since the two distinct processes cannot both be simple proton injection, our results show clearly that other processes can accomplish coloration in AIROF's. This opens up the possibility that a wide variety of processes might produce such coloration. Moreover, both isotherms are dominated by internal entropy changes of *noninteracting particles*. Such isotherms are qualitatively different from that of the proton-injection process in amorphous WO_3 electrochromics.

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[19]Cyclic voltammetry is a standard technique for studying electrochemical reactions in which the potential of the electrode is changed with time in a triangular waveform. The current is measured throughout the cycle and is plotted against the instantaneous potential. This current-voltage plot is called voltammogram.

[20]See, e.g., K. J. Vetter, *Electrochemical Kinetics* (Academic, New York, 1967), p. 717ff.

[21]Quantitative interpretations of the shapes of voltammograms are extremely rare and "except for diffusion controlled reactions, their interpretations leave much to be desired." Quoted from H. Angerstein-Kozlowska, J. Klinger, and B. E. Conway, J. Electroanal. Chem. 75, 45 (1977). In our case a quantitative interpretation is possible because the voltammograms are related directly to internal emf.

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