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Thin films of Co_3O_4 and $NiCo_2O_4$ obtained by the method of chemical spray pyrolysis for electrocatalysis III. The electrocatalysis of oxygen evolution

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The electrocatalytic properties of thin Co_3O_4 and $NiCo_2O_4$ films prepared on CdO-nonconductive glass by the method of chemical spray pyrolysis were investigated for oxygen evolution in varying KOH concentrations. The Tafel slopes were close to $(2.3RT/F)$ V per decade for both oxides. The reaction order with respect to $[OH^-]$ was found to be approximately 1.3. It was observed that Co_3O_4 is more active than $NiCo_2O_4$ towards oxygen evolution. A mechanism for oxygen evolution involving the electrochemical adsorption of OH^- as a fast step and the electrochemical desorption of OH forming an intermediate H_2O_2 as the rate-determining step has been suggested.

1. Introduction

Studies on the physico-chemical and electrochemical catalytic properties of complex oxides with the spinel structure, particularly Co_3O_4 and $NiCo_2O_4$ have received considerable attention during recent years [1–9], as they are low cost, easily available, reasonably stable and catalytically active materials. The investigations have been especially carried out on thin films of these oxides obtained on suitable substrates (both conducting and non-conducting) with [1–3] and without [4–9] an intermediate layer of a conductive oxide. Although various preparation procedures are known [10], in most of the investigations the oxides have been synthezised by thermal decomposition of the salts.

In Parts I and II of this work [11, 12], the method of chemical spray pyrolysis has been described for the first time to obtain the thin film electrodes of Co_3O_4 and $NiCo_2O_4$, and the details of their preparation, and physico-chemical and cyclic voltammetric studies have been reported. This method is quite simple, less time consuming and economical. Its main interest lies in the fact that it provides a way of obtaining well defined and structurally controlled materials as thin films which can be studied, with respect to their electrocatalytic properties, without need for any binding or conductive agent. The films of Co_3O_4 and $NiCo_2O_4$ so obtained were uniform and satisfactorily adherent to the substrate; their conductivity was found to be $10^2 - 10^4$ times higher than that observed with films prepared by other methods [11].

We now present the results of investigations on the electrocatalysis of oxygen evolution on these films in alkaline medium.

2. Experimental details

On a non-conductive glass (1 cm × 2.6 cm × 0.1 cm), successive layers of highly conductive CdO (acting as the charge collector) and Co_3O_4 (or $NiCo_2O_4$) were obtained by the chemical spray pyrolysis technique. The experimental set-up and the details of chemicals and their solutions used in the preparation of the films are described elsewhere [11, 13]. The furnace was regulated to give a constant temperature of 400 ± 10° C above the glass surface during the spray process. Air was employed as the carrier gas and its pressure was maintained constant at 2 bar. The flow rate of solution was adjusted to nearly 4 ml min^{-1} without altering the pressure of the air.

The formation of the compound concerned was checked by powder X-ray diffraction technique. The surface morphology of the films as deposited on the CdO-nonconductive glass substrate was examined under varying conditions by a scanning electron microscope (SEM) (Jeol).

For the electrochemical studies, an electrical contact between the oxide surface and the charge collector (CdO) was made with the help of a conductive silver paste. Only a 1 cm × 1 cm surface area of the oxide film was used for the study and the rest was isolated with a glue (Araldite).

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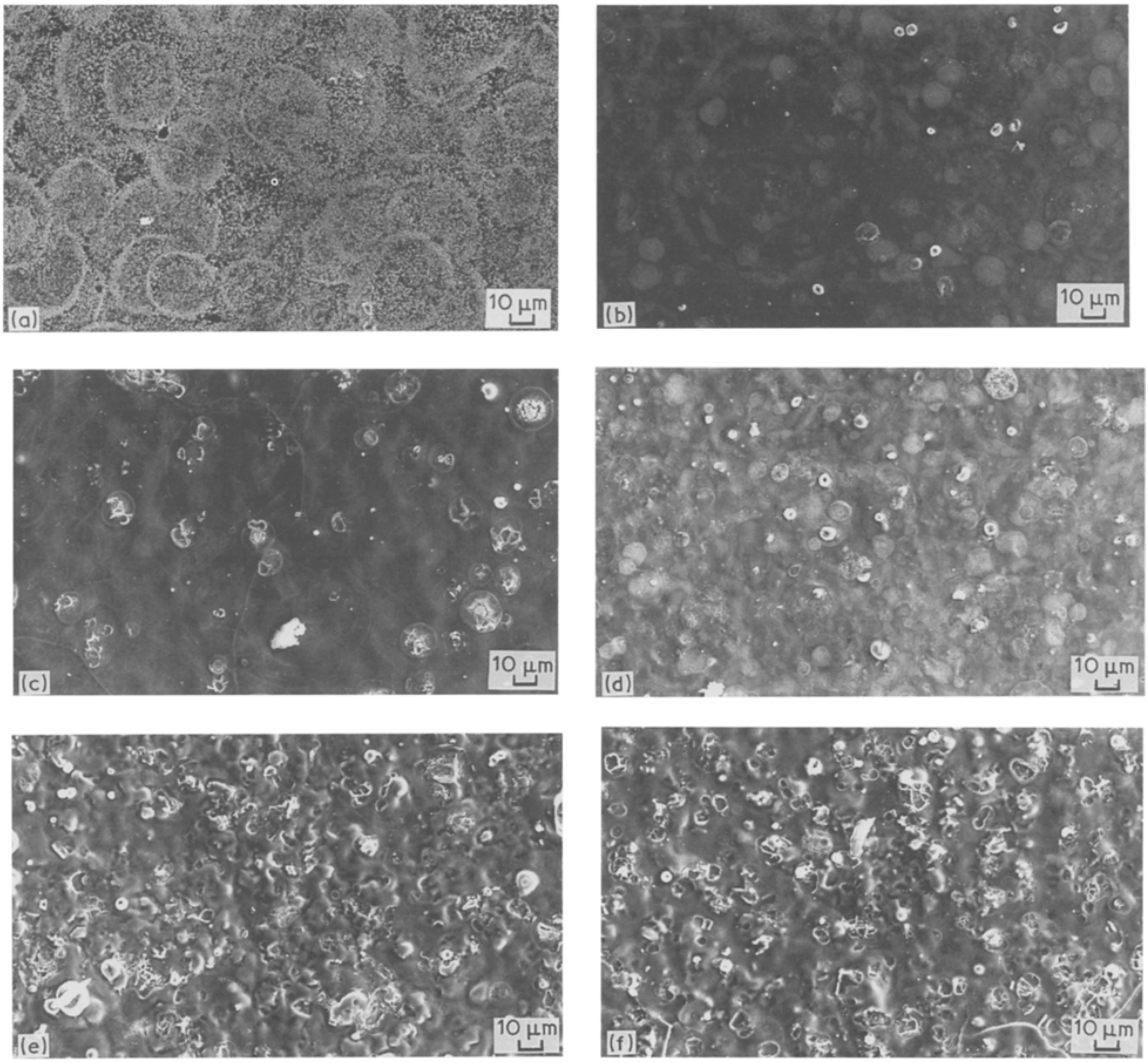

Fig. 1. SEM micrographs for: (a) freshly prepared CdO on glass; (b) and (c) freshly prepared Co_3O_4 and $NiCo_2O_4$ on CdO-glass, respectively; (d) and (e) Co_3O_4 and $NiCo_2O_4$ on CdO-glass after anodic polarization for 2 h at 1.4 V in 1 M KOH, respectively; and (f) $NiCo_2O_4$ on CdO-glass after 2 h immersion in H_2O.

The experiments were performed in a 200 ml Pyrex glass cell having provision for holding working, counter (bright Pt coil) and reference (Hg/HgO) electrodes and for introducing a gas (O_2/Ar). Electrode kinetic parameters were obtained by determining potentiostatic anodic and cathodic polarization curves using a potentio-galvanostat (Bruker, EI30 M).

Before the polarization studies, the electrode was anodized at 1.4 V for 30 min and then brought to the open circuit condition. After 15 min or so, the electrode potential was varied in steps of 20 mV in the direction of increasing overpotential and a steady value of current corresponding to each potential was noted. The time to reach a steady value was usually 2 min in the case of Co_3O_4 and 3–4 min for $NiCo_2O_4$. Distilled water was used for the preparation and dilution of KOH (Merck) solutions. 80 ml of KOH was used in the cell.

3. Results and discussion

3.1. *Morphology:*

SEM photographs of the CdO film on glass and the Co_3O_4 and $NiCo_2O_4$ films on glass with an inner layer of sprayed CdO in Fig. 1 indicate that the crystalline structure of CdO is fully masked by the active oxide overlayer. It was noted that the morphology of the Co_3O_4 film is unaffected by the contact with KOH solution and, further, by the anodic polarization (Fig. 1d). On the contrary, the morphology of the $NiCo_2O_4$ film was observed to be modified (blistered) by simply dipping into distilled water for 2 h (Fig. 1f). However, the modification thus obtained did not change further to any noticeable extent during the anodic polarization (Fig. 1e).

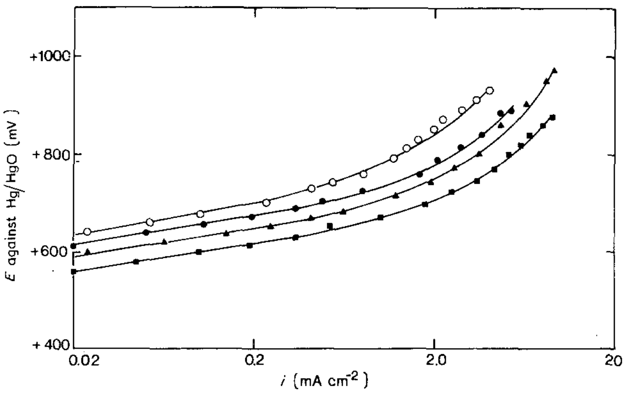

Fig. 2. Oxygen evolution on thin sprayed Co_3O_4 film on CdO-glass at varying KOH concentrations at 25° C, (○) 0.5 M KOH, (●) 1.0 M KOH, (▲) 2.0 M KOH, (■) 4.0 M KOH.

3.2. *Steady state polarization curves:*

The steady state current-potential data obtained for oxygen evolution on thin Co_3O_4 and $NiCo_2O_4$ films at different concentrations of KOH are shown in Figs 2 and 3. Each curve in these figures has been corrected for iR, where R is the resistance of the oxide electrode. Values of the resistance were determined by impedance measurements and found to be ~ 30 and ~ 20 ohms for Co_3O_4 and $NiCo_2O_4$, respectively. Current densities are expressed with respect to geometric surface area.

Figs 2 and 3 show that the Tafel lines are almost linear in the lower current density region and that the slope becomes increasingly steep in the higher current density region regardless of KOH concentrations. In the case of Co_3O_4, the region of linearity extended up to a current value of $\sim 0.5\,\mathrm{mA\,cm^{-2}}$ while for $NiCo_2O_4$ this was $\sim 0.8\,\mathrm{mA\,cm^{-2}}$ in 1 M KOH. The Tafel slope values were approximately 60 and 55 mV per decade for Co_3O_4 and $NiCo_2O_4$, respectively, in all four concentrations of the electrolyte used for the study, which indicates that the rate-determining step for oxygen gas evolution on either oxide is the activation controlled process involving one electron transfer. The increase of the Tafel slope in the higher current density region indicates a change in the rate-determining step in the oxygen evolution mechanism.

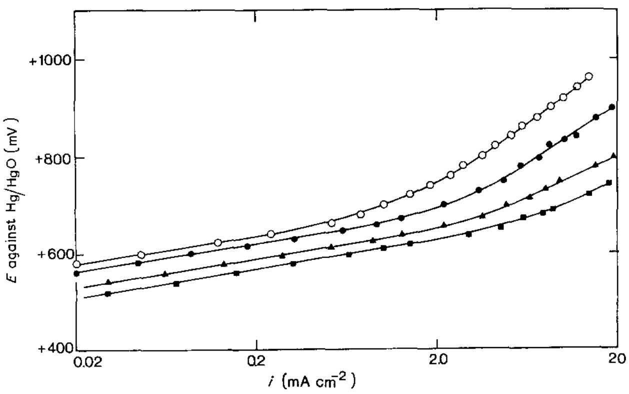

Fig. 3. Oxygen evolution on thin sprayed $NiCo_2O_4$ film on CdO-glass at varying KOH concentrations at 25°C, (○) 0.5 M KOH, (●) 1.0 M KOH, (▲) 2.0 M KOH, (■) 4.0 M KOH.

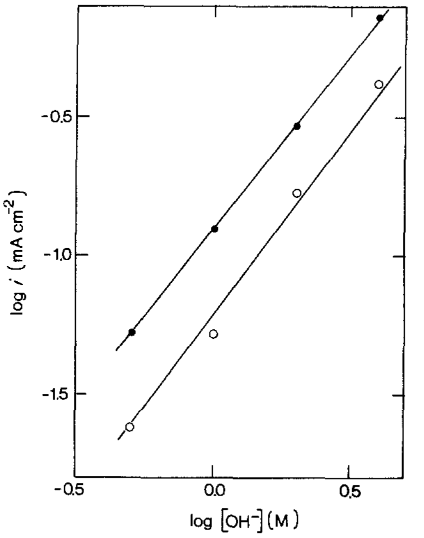

Fig. 4. log i against log [OH^-] plots at constant potentials from Fig. 2. (○) $E = +640$ mV, slope $= 1.3$, (●) $E = +660$ mV, slope $= 1.2$.

However, this is not so clear as the electrode surface was observed to be covered by gas bubbles, which may block some electrochemically active surface area. The latter process may also result in a higher slope.

The reaction order with respect to [OH^-] was determined from the slope plots of log i against log [OH^-] (Figs 4 and 5) and it was found to be approximately 1.3 for both oxides.

Oxygen evolution on Co_3O_4 and $NiCo_2O_4$ films has been studied by several workers. Depending upon the method, the experimental conditions and the nature of supports employed in the preparation of the films, varying values of the Tafel slope and of the reaction order with respect to [OH^-] were found. Rasiyah and Tseung [5] observed Tafel slopes of 60 mV per decade and second order kinetics in [OH^-] on Co_3O_4 and Li-doped Co_3O_4 Teflon-bonded anodes while they found [6] a Tafel slope of 120 mV per decade and first order kinetics on a $NiCo_2O_4$ Teflon-bonded anode. Similarly, for Co_3O_4 films supported on Fe and Pt, Iwakura *et al.* [4] reported Tafel slopes of 45 and

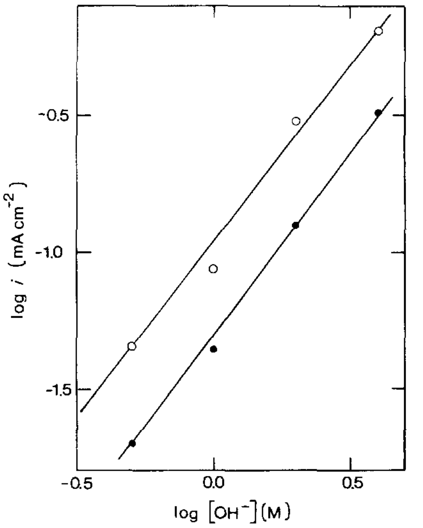

Fig. 5. log i against log [OH^-] plots at constant potentials (1.3) from Fig. 3. (●) $E = +580$ mV, slope $= 1.3$ (○) $E = +600$ mV, slope $= 1.3$.

55 mV per decade, respectively, whereas for similar films supported on Ti, Co, Ni, Nb and Ta the Tafel slope values ranged between 58 and 64 mV per decade. However, in each case, first order kinetics in $[OH^-]$ were observed. On the other hand, similar studies conducted by Burke and McCarthy [9] and by Carugati and Trasatti [14] on Co_3O_4/RuO_2 electrodes supported on Ti and on $NiCo_2O_4$ showed a Tafel slope of 40 mV per decade with both oxides.

In the present study the values of the kinetic parameters suggest that oxygen evolution follows similar mechanistic paths for both oxides. Cyclic voltammetric studies, as reported earlier [1, 12, 15], have demonstrated that before oxygen evolution the surface of cobaltites is oxidized to tetravalent oxidation states (namely, Co(IV) or Ni(IV)) and that no further oxidation takes place during oxygen evolution. Further, coulometric studies on $NiCo_2O_4$ indicated [15] a maximum oxidation state of +4 for cobalt or nickel in the spinel lattice.

Considering the above results, we suggest the following mechanism for O_2 evolution on sprayed Co_3O_4 and $NiCo_2O_4$ films:

$$S^{IV} + OH^- \rightleftharpoons S^{IV} - OH + e^- \qquad (1)$$

$$S^{IV} - OH + OH^- \xrightarrow{\text{rds}} S^{IV} \ldots H_2O_2 + e^- \qquad (2)$$

The physisorbed H_2O_2 thus formed decomposes [16, 17] catalytically in subsequent fast chemical steps finally yielding O_2. The sum of the steps can be represented as follows:

$$2S^{IV} \ldots H_2O_2 \longrightarrow 2S^{IV} + 2H_2O + O_2\uparrow \qquad (3)$$

where S^{IV} ($= Co^{IV}$ or Ni^{IV}) is an active site on the oxide surface.

Similar mechanisms have recently been proposed for oxygen evolution on perovskites [18, 19]. The formation of H_2O_2 as an intermediate has also been suggested on oxygen photoanodes [20, 21].

The proposed mechanism agrees with the experimental data if it is assumed that the coverage of oxide electrodes by adsorbed intermediates (that is oxygen containing species) is appreciable and influences the heats of adsorption and hence the free energies of activation of species to be adsorbed. Under this condition, for an adsorption-desorption process the following relationship between the apparent equilibrium constant (K) and the total coverage (θ_T) is found to hold well [22]:

$$K = K^\circ \exp\left(-\frac{r\theta_T}{RT}\right) \qquad (4)$$

where K° is the standard equilibrium constant for the adsorption-desorption process and r is a coefficient determining the variation of the heat of adsorption with θ_T.

According to Equation 4, the rate of the adsorption step decreases while the rate of the desorption step increases with increase in θ_T. Thus, the rate of O_2 evolution from reaction (2) can be written as

$$v = v_2 = k_2^\circ\theta_{OH}C_{OH^-} \exp\left(\frac{\alpha r\theta_T}{RT}\right) \exp\left(\frac{\beta FE}{RT}\right) \qquad (5)$$

Where α and β are symmetry factors and E is the electrode potential with respect to a reference electrode (namely Hg/HgO).

Assuming the adsorption-desorption process (1) to be in a quasi-equilibrium condition and $\theta_T \simeq \theta_{OH}$, one obtains the following relation at intermediate values of the coverage ($0.2 < \theta_{OH} < 0.8$).

$$\theta_T = \frac{RT \ln K_1^\circ C_{OH^-}}{r} + \frac{EF}{r} \qquad (6)$$

Now, substituting the value of θ_T in Equation 5, the final expression for rate becomes

$$v = k_2^\circ\theta_{OH}C_{OH^-} \exp\left[\frac{\alpha}{RT}(RT \ln K_1^\circ C_{OH^-} + FE)\right] \times \exp\left(\frac{\beta FE}{RT}\right) \qquad (7)$$

Considering that θ_{OH} is relatively invariant under intermediate coverage conditions and that $\alpha \simeq \beta \simeq 0.5$, Equation 7 gives a Tafel slope and reaction order with respect to $[OH^-]$ as approximately 2.3 RT/F and 1.5, respectively.

The Tafel slope value and the reaction order so obtained are in close agreement with those found experimentally. Further, it is known [23] that Temkin conditions generally prevail over a narrow range of overpotentials (~ 150 mV). The polarization curves determined in the present study (Figs 2 and 3) also indicate a small overpotential region (~ 100 mV) for the Tafel slope of RT/F, thus, clearly substantiating that the linear Tafel region is due to Temkin adsorption conditions.

From the polarization curves (Figs 2, 3) it seems that the $NiCo_2O_4$ anode is more active than Co_3O_4. In fact, the latter electrode is more active as the current densities, in terms of the real surface area, were found to be roughly twice those observed in the case of the former (Table 1). This indicates that the Co(IV) sites produced from the oxidation of Co(III), during the anodic polarization conditions, are the active sites for O_2 evolution. The decrease in the activity of $NiCo_2O_4$ may be attributed to the decrease of the Co(III) sites by nearly one half in the spinel lattice of $NiCo_2O_4$ as reported elsewhere [11].

The stability of the oxide electrodes has also been examined by anodizing at a current density of 25 mA cm^{-2} in 5 M KOH for times up to 40 h. The potentials measured at different time intervals are shown in Fig. 6 which shows that the potential of the working electrode increases gradually by nearly 220 mV during the first 20 h or so and becomes almost constant thereafter. After the test was over, further anodic polarization studies were made on these electrodes in 1 M KOH; the results showed the same Tafel slope as obtained before. However, the activity of the electrodes was slightly diminished.

Table 1. Current densities based on real surface areas for oxygen evolution at $E = +700\,mV$ Hg/HgO

Electrode	*Apparent current density* $(mA\,cm^{-2})$			*Roughness factors*	*True current density* $(mA\,cm^{-2})$		
	[KOH], M				*[KOH], M*		
	1	2	4		1	2	4
Co_3O_4	0.48	0.96	1.8	5*	0.096	0.192	0.36
$NiCo_2O_4$	2.2	5.0	9.8	55*	0.04	0.091	0.178

*Refs [11]

4. Conclusions

This study has confirmed that oxygen evolution occurs preferentially on the Co(IV) sites on oxide surfaces. On the basis of the estimation of the relative real surface areas, which is rendered possible here by the use of films of the pure materials, without conductive and binding agents, it was found that $NiCo_2O_4$ is less active than Co_3O_4. The smaller activity of $NiCo_2O_4$ can be attributed to the decrease of the Co(III) sites (which are the major source for the active Co(IV) sites) in the spinel lattice of $NiCo_2O_4$. Oxygen evolution follows similar mechanisms on both oxides.

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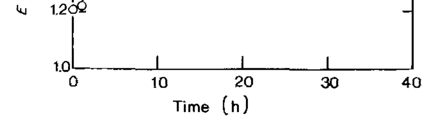

Fig. 6. The stability test data for oxide electrodes in 5 M KOH at 25°C and $i = 25\,mA\,cm^{-2}$ under galvanostatic condition, (●) Co_3O_4, (○) $NiCo_2O_4$.

References

[1] R. Boggio, A. Carugati and S. Trasatti, *J. Appl. Electrochem.* **17** (1987) 828.
[2] S. Trasatti, *Electrochim. Acta* **29** (1984) 1503.
[3] I. Vartires, A. Mihelis, V. Popescu and N. Spătaru, *Revue Roumaine de Chimie* **32** (1987) 551; *ibid* **32** (1987) 907.
[4] C. Iwakura, A. Honji and H. Tamura, *Electrochim. Acta* **26** (1981) 1319.
[5] P. Rasiyah and A. C. C. Tseung, *J. Electrochem. Soc.* **130** (1983) 365.
[6] *Idem, ibid.* **130** (1983) 2384.
[7] A. Carugati, G. Lodi and S. Trasatti, *J. Electroanal. Chem.* **143** (1983) 419.
[8] C. Pirovano and S. Trasatti, *ibid.* **180** (1984) 171.
[9] L. D. Burke and M. M. McCarthy, *J. Electrochem. Soc.* **135** (1988) 1175.
[10] M. R. Tarasevich and B. N. Efremov, in 'Electrodes of Conductive Metallic Oxides' Part A (edited by S. Trasatti), Elsevier, New York (1980) p. 223.
[11] M. Hamdani, J. F. Koenig and P. Chartier, *J. Appl. Electrochem.* **18** (1988) 561.
[12] *Idem, ibid.* **19** (1988) 568.
[13] L. Bahadur, M. Hamdani, J. F. Koenig and P. Chartier, *Solar Energy Materials* **14** (1986) 107.
[14] A. Carugati and S. Trasatti, 33ème I.S.E., Lyon 1982.
[15] P. Rasiyah and A. C. C. Tseung, *J. Electrochem. Soc.* **129** (1982) 1724.
[16] O. Spalek, J. Balej and I. Paseka, *J. Chem. Soc. Faraday Trans. I* **78** (1982) 2349.
[17] S. K. Tiwari and R. N. Singh, *Ind. J. Chem.* **26** (1987) 420.
[18] A. G. C. Kobussen and G. H. J. Broers, *J. Electroanal. Chem.* **126** (1981) 221.
[19] J. O'M. Bockris and T. Otagawa, *J. Phys. Chem.* **87** (1983) 2960.
[20] P. Salvador, *J. Electrochem. Soc.* **128** (1981) 1895.
[21] P. Clechet, C. Martlet, J. R. Martin and R. Olier, *J. Electrochim. Acta* **24** (1979) 457.
[22] E. Gileadi, E. Kirowa-Eisner and J. Penciner, 'Interfacial Electrochemistry', Addision-Wesley, Reading, Massachusetts (1975) p. 82.
[23] A. Damjanovic in 'Modern Aspects of Electrochemistry', Vol. 5 (edited by J. O'M. Bockris and B. E. Conway), Plenum, New York (1969) p. 369.