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Surface Chemistry of Oxides and Electrocatalysis*

Sergio Trasatti

Department of Physical Chemistry and Electrochemistry, University of Milan, Via Venezian 21, 20133 Milan, Italy

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After an introductory description of the moment acquired by some oxide electrodes in the electrochemical technology, the procedure for their preparation and the physicochemical and electrochemical characterizations are described emphasizing the interdisciplinary character of the research in this field. The importance of separating geometrical from electronic parameters for a proper understanding of the factors governing the electrocatalytic activity is stressed. Arguments along these lines lead to the association of electrocatalysis with surface acid-base dissociation concepts. A parallel analysis of the behaviour of the point of zero charge and of the electrocatalytic activity for the anodic evolution of oxygen shows that the former property can be used as a diagnostic, intensive parameter for a relative evaluation of the electrocatalytic activity of a set of oxide electrodes. Results for RuO_x, IrO_x, Co_3O_4 and $NiCo_2O_4$ are discussed.

INTRODUCTION

The understanding of the behaviour of electrode/electrolyte interfaces calls for an interdisciplinary background and multiple experimental approaches. Solid state and surface chemistry and physics have thus become necessary tools for electrochemists especially when working in the field of interface structure and electrocatalysis.[1]

Electrochemistry deals with the conversion of electrical into chemical energy (electrolyzers) and *vice versa* (power sources). Materials, chemicals and energy all have dramatic technological impact. Technological advancement calls for innovative ideas ultimately aiming at reducing the operationl costs. This is only possible if the conversion of energy is operated with better efficiency.

Better efficiency is basically a problem of materials. Let's examine the case of electrolyzers. The external voltage applied to an electrolyzer to drive the wanted reactions can be split into several components:

$$\Delta V = E_a - E_c + \eta_a + \eta_c + \Delta V_\Omega + \Delta V(t) \tag{1}$$

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where E is the thermodynamic (reversible) electrode potential, η is the overpotential (necessary to drive the reaction at a practical rate), ΔV_Ω is the total ohmic loss in the structure, the electrodes and the interelectrode gap (solution), and $\Delta V(t)$ can be termed *»stability«* and represents any possible drift in the previous parameters resulting in a time dependence of ΔV.

Since the energy efficiency:

$$\varepsilon = \Delta E/\Delta V \tag{2}$$

must be maximized to keep operational costs down, ΔV must be minimized. ΔE cannot be changed so long as the processes at the two electrodes remain the same (*e. g.*, evolution of Cl_2 and H_2 in a chlor-alkali cell, evolution of O_2 and H_2 in a water electrolysis cell, *etc.*); therefore, η, ΔV_Ω and $\Delta V(t)$ are the parameters which the technological research aims at reducing as much as possible.

Overpotentials mainly depend on the nature of the electrode materials;[2] the purpose of *electrocatalysis* as a science is to establish a predictive basis for the design and te optimization of electrode materials. By a suitable selection of materials, it is possible in principle to influence η. ΔV_Ω depends essentially on the cell design. It is the task of electrochemical engineering to minimize this parameter.[3] Finally, $\Delta V(t)$ is mainly a function of electrode materials, but it can also be influenced by the operating conditions and the cell design. It is at the same time the most important (an active but unstable material is technologically useless) and the most difficult parameter to control. In this paper, we shall focus on the relation between the surface properties and the corresponding electrocatalytic activity of materials.

OXIDE ELECTRODES

Electrode materials must possess a number of qualities to be of interest in the electrochemical technology: large surface area, high electrocatalytic activity, long-term stability, high electrical conductivity, *etc.* Materials meeting all the requirements at best are of course difficult to find. However, in the sixties, Beer[4] discovered that the electrochemical performances of some transition metal oxides are substantially better than those of the parent metals. In particular, besides extremely interesting electrotalytic properties, these oxides exhibit an exceptional stability under the most severe conditions of use.

DSA

The acronym DSA is universally used to indicate the oxide electrodes used as anodes for a variety of electrode processes: chlor-alkali, cells, water electrolysis, metal electrowinning, organic electrosyntheses, *etc.* The term *Dimensionally Stable Anodes* emphasizes their stability towards chemical and electrochemical deterioration. Basically, they consist of active transition metal oxides (RuO_2, IrO_2, Co_3O_4, perovskites, *etc.*) stabilized by valve metal oxides (typically TiO_2, but also ZrO_2, Ta_2O_5, *etc.*) and deposited as a thin layer (a few microns thick) on an inert support (mostly Ti in technological applications). 1989 has marked the 25 years from the introduction of DSA into the electrochemical industry; the event has been celebrated by the Electrochemical Society with a special symposium.[5]

Preparation

Although oxides can be prepared by various procedures, thermal decomposition of suitable precursors is the most convenient method to prepare practical electrodes[6] since it lends itself especially well to deposit layers on supports. Precursors are $RuCl_3$ and $IrCl_3$ for RuO_2 and IrO_2, respectively, Ni and Co nitrates for spinels, *etc.* Thermal decomposition takes place in a wide range of temperature, mostly between 300 and 500 °C. Since the process is substantially a fast, low temperature calcination, non-stoichiometric oxides are usually obtained. Thus, RuO_x is oxygen deficient,[7] whereas oxygen in excess is present in Co_3O_{4+x}.[8] Non-stoichiometry turns out to be a function of temperature with the defect concentration decreasing as the calcination temperature is increased. In some cases residues of the precursors may remain in the lattice.[9] This is shown in Figure 1, where the Cl content of RuO_x can be seen to decrease with temperature in a way substantially independent of the macroscopic morphology (*i. e.*, the appearance of the layer surface on the SEM).

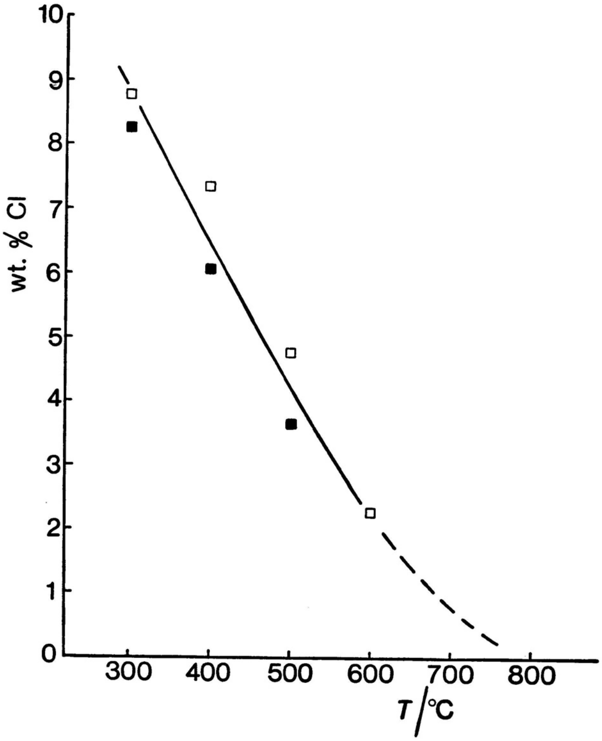

Figure 1. Chlorine content of RuO_x layers prepared by thermal decomposition of $RuCl_3$ at various temperatures. Macroscopic morphology as visible on the SEM: (■) Cracked; (□) Compact layers.

Surface Structure

The microscopic morphology is also a function of the calcination temperature. Figure 2 shows that the BET surface area of Co_3O_4 has been found to decrease monotonically with the temperature of decomposition of $Co(NO_3)_2$ in much the same way in different laboratories.[8] This behaviour is well known in catalysis and is related to crystallite growth and sintering as the temperature rises.

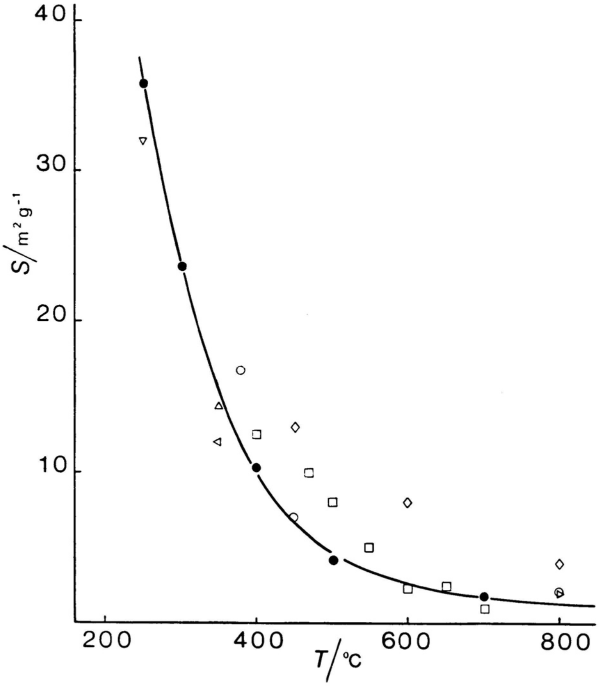

Figure 2. BET surface area of Co_3O_{4+x} powders prepared by thermal decomposition of $Co(NO_3)_2$ at various temperatures. Different symbols refer to data from different laboratories. (●) This laboratory.

In order to deposit the precursor onto the support, the salt is dissolved in an appropriate solvent. Results have shown that changing the solvent influences the crystallite size at a given calcination temperature.[10] Therefore, several factors turn out to influence the features of the oxide layer: nature of the precursor and of the solvent in which it is dissolved, calcination temperature and time of firing, procedure of precursor deposition, *etc.* This clearly emphasizes how necessary is a proper characterization of the surface state of the oxide layer in order to be able to relate it to the electrocatalytic activity.

The evidence accumulated by means of solid state and surface structural investigations has suggested that the layer constituting the active part of oxide electrodes possesses the morphology tentatively depicted in Figure 3. The layer resembles a wall made of bricks (crystallites) held together by amorphous concrete (highly defective grain boundaries). Pores may also be present.

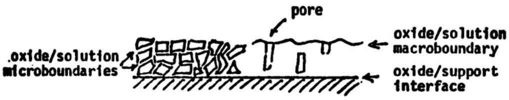

Figure 3. Sketch of the morphology of an oxide layer. Crystallites are separated by highly defective regions (loose grain boundaries). Pores may also be present. The different kinds of interfaces are indicated.

Surface Hydration

As oxides are in solution, three interfaces can be recognized (Figure 3): *(i)* the oxide/solution macroboundary characterized by the macroscopic external surface, *(ii)* oxide/solution microboundaries along the pore walls and the intercrystallite gaps, and *(iii)* the boundary at the oxide/support interface which may have a substantial influence on the electrode performances since a film of insulating TiO_2 may developed on the support surface. While the features of the external macroboudary where formation of an OH »carpet« on the oxide surface due to chemisorption of water molecules takes place are well understood,[11] microboundaries are thought to exist because a substantial penetration of hydrogen has been detected by nuclear techniques.[12] Figure 4 shows that a RuO_x layer becomes hydrated in depth by simply staying in the dampness of the lab atmosphere. After immersion in boiling water, the hydrogen profile has been found to follow the Ru profile. However, the [H]/[Ru] ratio has been calculated to be only *ca.* 0.05, which suggests that the Ru atoms in the bulk of crystallites are not hydrated. It ensues that the ratio is too high to be determined only by hydration of the oxide/solution macroboundary.

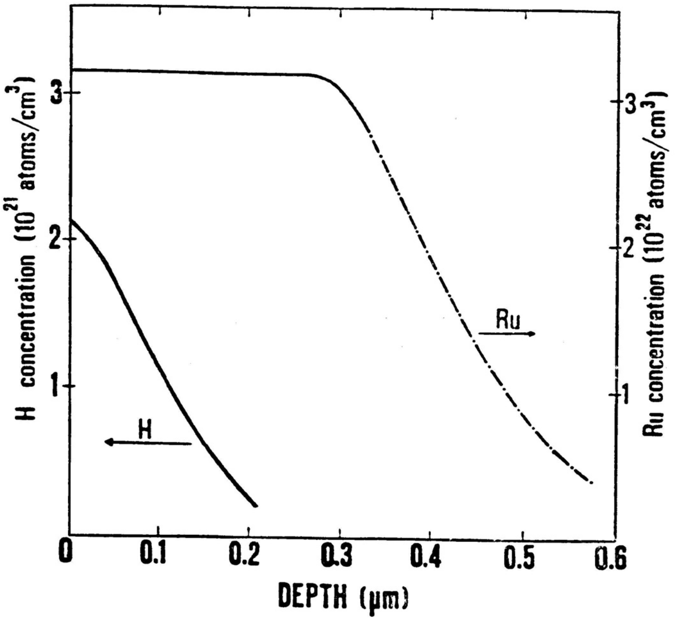

Figure 4. H and Ru profiles through a RuO_x layer kept in the laboratory atmosphere.

The presence of OH groups »below« the macroscopic external surface have been revealed also by XPS.[13] The most direct evidence for proton penetration has however been provided by tritium exchange. Marked RuO_2 exchanges tritium in a way indicating the presence of a diffusion step (Figure 5). The amount of tritium exchanged after a given time minus the amount excanged at $t = 0$ (corresponding to the external surface only) gives the amount of tritium exchanged in subsurface regions. Figure 5 shows that the amounth of »internal« tritriated sites decreases with the calcination temperature in a way resembling the surface area. This is not surprising, since both quantities depend on the crystallite size.

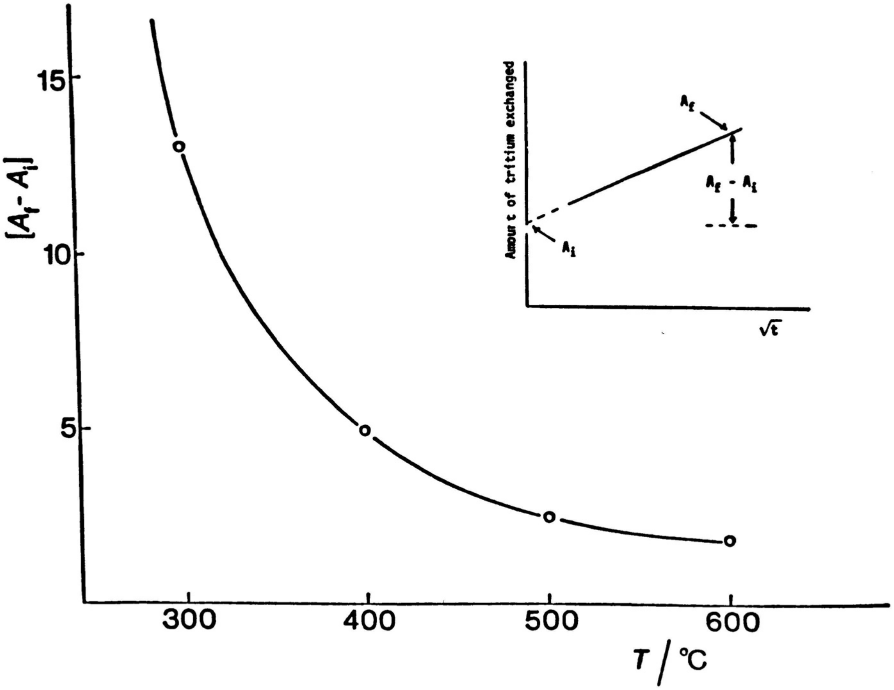

Figure 5. Tritium exchange ability of RuO_x layers prepared by thermal decomposition of $RuCl_3$ at various temperatures. A_i is the amount of tritium exchanged at $t \to 0$; A_f is the amount after longer times. (A_f—A_i) is the amount of tritium in the »bulk« of the oxide.

Surface Charge and Surface Area

The *in situ* characterization of oxide electrodes is best performed by cyclic voltammetry (CV). This technique consists in applying a programmed potential scan to the electrode and in recording the surface response as an electric current. In terms of molecular interactions at the electrode surface, this technique can be conceptually compared with the TDS (thermal desorption spectroscopy). In TDS the temperature varies the energy of the molecules adsorbed on the surface; in CV the potential varies the energy of the electrode surface. In both cases peaks are obtained which can be interpreted in terms of adsorption-desorption phenomena. In this respect the curve recorded by CV is often referred to as an »*electrochemical spectrum*«.

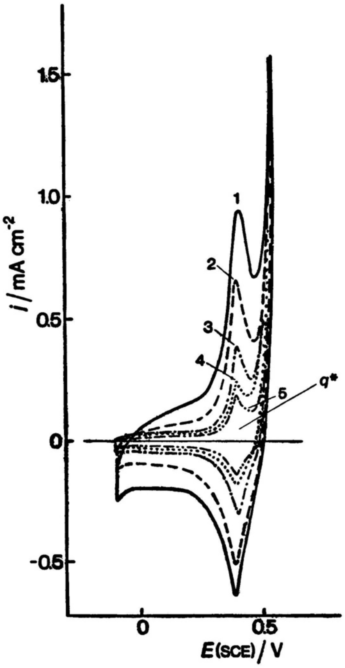

Figure 6. Voltammetric curves of Co_3O_{4+x} layers calcined at various temperatures. q^* is the charge obtained by integration. (1) 230; (2) 260; (3) 300; (4) 400; (5) 500 °C.

Figure 6 shows the »eletrochemical spectra« of Co_3O_4 electrodes prepared at various temperatures. The potential range has been chosen so that no solvent decomposition (resulting in H_2 or O_2 formation) takes place. The direction of potential scan in the anodic direction is reversed just prior to the start of oxygen evolution. Under similar circumstances, the current recorded is solely due to oxidation-reduction of surface sites according to the general equation:

$$MO_x(OH)_y + \delta H^+ + \delta e^- \leftrightarrow MO_{x-\delta}(OH)_{y+\delta} \quad (2)$$

Equation (2) shows that the charge spent for oxidizing or reducing surface sites measure the number of protons exchanged between the oxide surface and the solution (proton exchange accompanies the redox reaction). The charge q^* obtained by integration of the voltammetric curve turns out to be a parameter proportional to the number of active sites, *i. e.* to the electrochemically active surface area. Therefore, voltammetric curves can be used as powerful tools to monitor *in situ* the state of the surface of oxide electrodes at any time of their life.

»Inner« and »Outer« Surface

Experimental data show[14] that q^* decreases as the calcination temperature increases (Figure 6), as expected for a surface area effect. The correlation between q^* and BET surface area is emphasized in Figure 7 where the two sets of data are however inhomogeneous in the sense that they do not refer to the same samples. On the other hand, the electrodes used in these studies are usually 1 × 1 cm platelets so that the area/volume ratio is not adequate for direct BET surface area measurements. BET data are normally taken with powder samples prepared with the same procedure at the same temperature. In this context, the slope of the correlation has no quantitative meaning while the correlation itself retains all its validity. In conclusion, q^* provides a relative measure of surface area, which is enough for electrocatalytic evaluations, intrinsically based on relative comparisons.

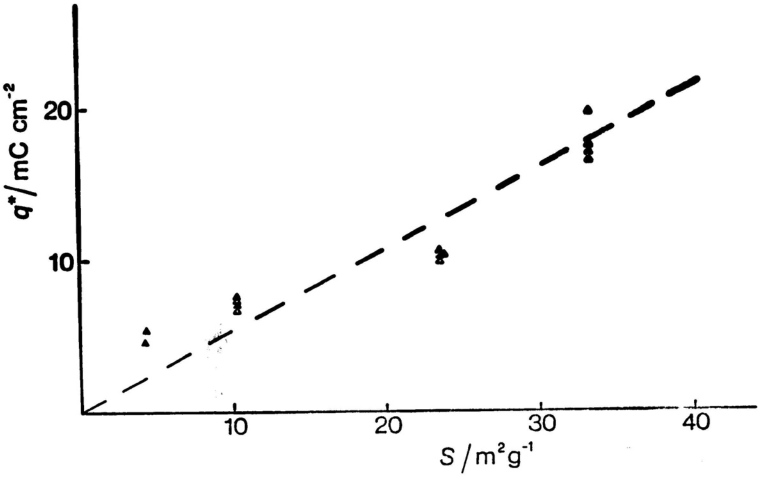

Figure 7. Correlation between q^* from CV and the BET surface area of Co_3O_{4+x} samples prepared at different temperatures. q^* measured with layers; S measured with powders.

The existence of »internal« surface active sites is pointed out by the dependence of q^* on the potential scan rate, v. q^* has been found to vary linearly with $v^{-1/2}$, which suggests that the proton exchange rate is limited by some steps of a diffusive nature. Figure 8 shows that q^* can be extrapolated to $v = 0$ if $1/q^*$ is plotted *vs.* $\sqrt{v}$, and to $v = \infty$ if q^* is plotted *vs.* $1/\sqrt{v}$. q_o^* measures the total active surface, while q_∞^* measures only the surface area which can exchange protons at high potential sweep rate. Therefore, q_∞^* is proportional to the »outer« macroscopic surface (*cf.* Figure 3) and is related to q_o^* by the equation:[15]

$$q_o^* = q_\infty^* + q_i^* \tag{3}$$

where q_i^* is proportional to the »inner« microscopic surface (*cf.* Figure 3) Experimental results have shown that the ratio q_∞^* / q_o^* is a constant irrespective of the calcination temperature: it is a feature of the given oxide. This is allustrated by Figure 9 where q_∞^* has been plotted against q_o^*.

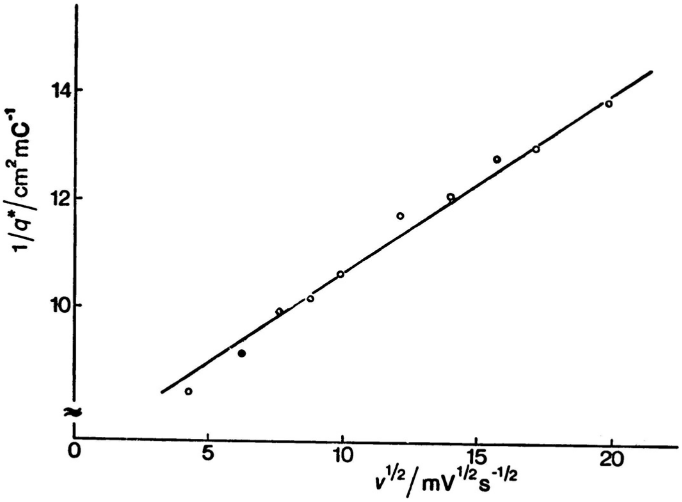

Figure 8. Typical plot of the reciprocal of q^* *vs.* the reciprocal of the square root of the potential scan rate for a RuO_x layer in $HClO_4$ solutions, showing the linear dependence.

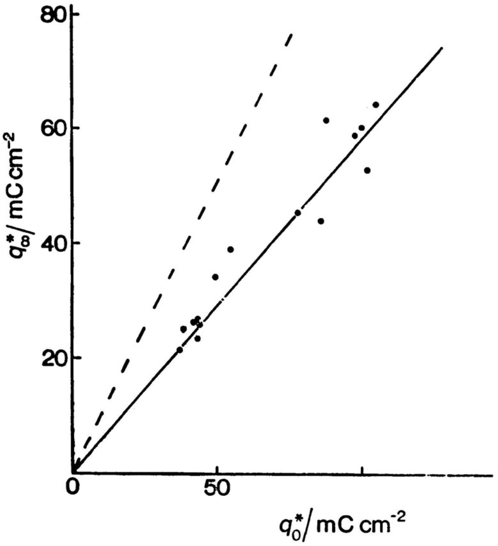

Figure 9. Correlation between q^* at $t \rightarrow 0$ and q^* at $t \rightarrow \infty$ (from plots as in Figure 8) for RuO_x layers prepared at various temperatures. (— — — · — — —) Unit slope.

Surface Composition

The parallelism between voltammetry and surface spectroscopies is demonstrated by the fact that the surface composition of mixed oxides (often used to modulate the catalytic activity of electrodes through synergistic effects) can be estimated by CV as accurately as it can be estimated by XPS or AES.[16] Figure 10 shows that the »electrochemical spectrum« of RuO_x is characterized by features different from that of IrO_x. In case of $RuO_x + IrO_x$ mixed oxides, a typical feature can be identified for each of the oxides (as a rule, the »height« of a peak), and used to derive a relative amount of that specific feature in the mixture, *i. e.* the relative amount of that given oxide. Figure 11 shows a comparison between the surface analyses by CV and XPS. It is clear that in this specific case CV can give results as reliable as XPS, with the advantage that the CV analysis can be carried out *in situ* at any time of the electrode life.

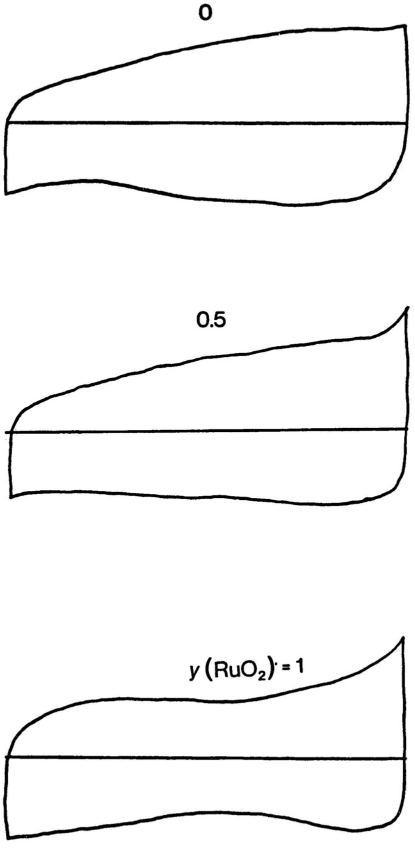

Figure 10. - Voltammetric curves for $yRuO_X + (1\text{-}y)\,IrO_X$ layers of different composition showing the evolution of the features.

GEOMETRIC AND ELECTRONIC FACTORS

The importance of surface area measurements in materials research for electrocatalysis can hardly be overemphasized. Evaluation of the electrocatalytic properties of a given material can only be made on a relative basis with respect to another material. In electrochemistry, the electrocatalytic activity is measured in terms of current *(j)* at a given potential *(E)*. Current is usually

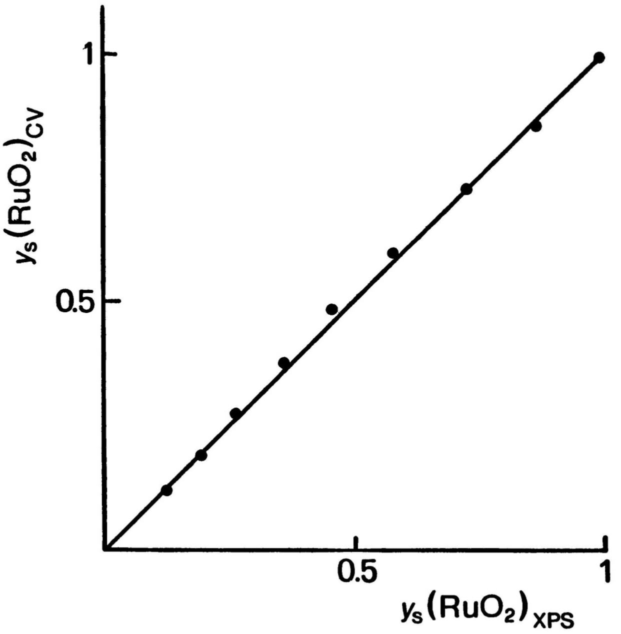

Figure 11. Surface composition of $yRuO_x$ + (1-y) IrO_x layers. Plot of the values derived by CV against those obtained by XPS. (———) Unit slope.

referred to the unit of apparent surface area so that both electronic and geometric effects contribute in fact to the apparent activity of an electrocatalyst. Hence, the importance of knowing the *real* surface area to be able to disentagle truly electrocatalytic (electronic) factors from mere surface area (geometric) effects.

Extensive and Intensive Parameters

The voltammetric charge q^* lends itself especially well in the case of oxide electrodes to be used as a purely real surface area parameter*. Of course, the approach cannot be exploited for a single point system, *i. e.* for a single electrode. In view of the relative significance of q^* and j (electrocatalytic activity), only a correlation over several points can be illuminating. Figure 12 shows the typical case of O_2 evolution on IrO_x electrodes. Each point refers to a different electrode prepared at a different temperature or with a different procedure. The range of q^* values cover more than one order of magnitude. In a plot of log j *vs.* log q^* a straight line of unit slope should be obtained, if only surface area effects are operating. Figure 12 shows that this is probably the case at low q^* (surface area) values but deviations are observed at higher q^* values. In particular, deviations are higher for the set of electrodes prepared by dissolving the precursor ($IrCl_3$) in water than for the set for which isopropanol was used. Therefore, definite evidence for real electrocatalytic effects is obtained especially for the former set of electrodes. The reason

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* Note that this approach is not a novelty in electrochemistry. Charges are used to estimate the real surface area of metal electrodes in many instances, notably Pt.[17]. The extension of this approach to oxide electrodes is new.

for that is probaly to be sought in the fact that as crystallites become smaller and smaller, edge effects become predominant. Crystallites of different structures are obtained in different solvents presumably as a consequence of different kinetics of decomposition.

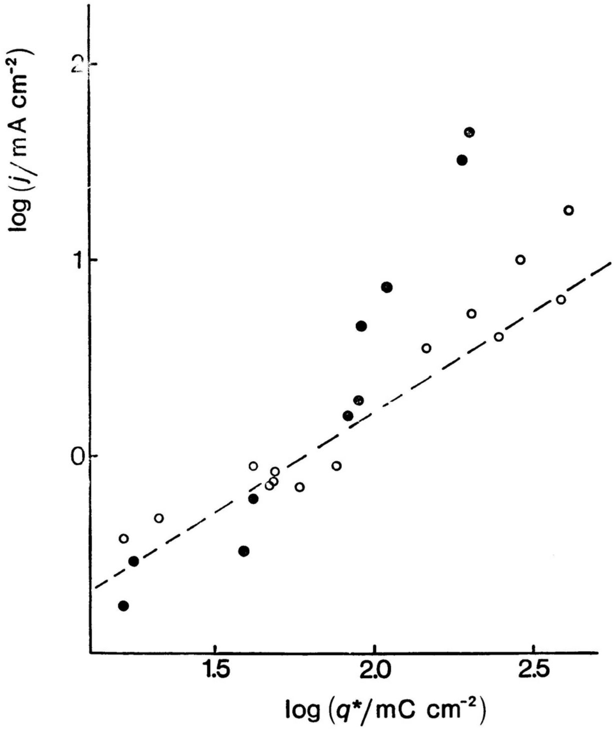


Figure 12. Log-log plot of the electrocatalytic activity (j) for O_2 evolution *vs.* the CV surface charge (q^*) for IrO_x layers prepared by thermal decomposition of $IrCl_3$ dissolved in water (●) or in isopropanol (o). (— — — —) Unit slope.

While such correlations as those in Figure 12 are very specific to disentangle electronic from geometric effects, their absolute validity may be affected by the following considerations: *(i)* the intrinsic accuracy of the two quantities j and q^* is not the same; *(ii)* q^* may also depend on the nature of the active sites and not only on their surface concentration; *(iii)* both j and q^* are extensive quantities. More reliable results would be obtained if the comparison quantity to discriminate between geometric and electronic factors were an intensive one.

Tafel Slope

Kinetic data can in fact provide such a quantity; it is the so-called *Tafel* slope.[18] If an electrode reaction is governed by the intrinsic activation energy related to the charge transfer step, the reaction rate (current) turns out to be exponentially related to the overpotential (η). It follows that η and ln j are linearly related by a coefficient which is the Tafel slope *(b)*:

$$\eta = b \ln (I/I_0) \qquad (4)$$

I_0 is the exchange current, *i. e.* the reaction rate at $\eta = 0$. I_0 (or I at constant η) is an *extensive* quantity and measures the electrocatalytic activity (*cf.* Figure 12); on the contrary, b is an *intensive* quantity and its value is determined by the reaction mechanism.[19] Electrochemistry is the only field where reaction mechanisms can be obtained by making measurements of reaction rates at a single temperature and a single concentration of reactants. This is a consequence of the extra degree of freedom provided by the possibility of controlling the electrode potential, *viz.* the energy of one of the reactants: the electrons.

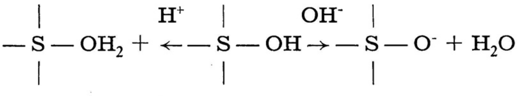
Although b is an intensive quantity, its relation to the electrocatalytic activity is not straightforward. In fact, if b changes along a series of electrodes, it is obvious that also the electrocatalytic activity changes since a modification in mechanism is normaly a result of different intermediate-catalyst interactions. However, if b is constant over a suries of electrodes, the electrocatalytic activity may be different at constant mechanism and we are back to the current as the only parameter which can allow a relative evaluation of activity. Thus, an additional experimental parameter is needed to improve the situation.

SURFACE ACID-BASE PROPERTIES

A third parameter can be borrowed from the field of the surface chemistry of oxides. The approach described below emphasizes the interdisciplinary character of electrochemistry and proves that two quantities, the point of zero charge and the electrocatalytic activity of an oxide surface, only apparently belong to different fields, while they are in fact governed by the same intrinsic factor, *viz.* the acid-base properties of the oxide/solution inferface.

Point of Zero Charge

The OH groups present on the surface of a wet oxide can undergo acid-base dissociation as weak acids or bases do:[11]



$$\mathrm{-\overset{|}{\underset{|}{S}}-OH_2^+} \xleftarrow{\mathrm{H^+}} \mathrm{-\overset{|}{\underset{|}{S}}-OH} \xrightarrow{\mathrm{OH^-}} \mathrm{-\overset{|}{\underset{|}{S}}-O^- + H_2O} \qquad (5)$$

Thus, in alkaline solutions oxide surfaces are negatively charged while they are positively charged in acidic solution. At a specific pH (pH_z or point of zero charge, pzc) the surface is electrically (and chemically) neutral. It is clear that since the acid-base properties depend on the nature of the M-OH interactions, the pzc is a property which depends on the nature of the active sites. Therefore, if for different samples of the same oxide the pzc varies, this is very likely to mean that the surface sites are different. The important feature of the pzc is that it is an *intensive* property.

We have thus found a property which can tell us when the nature of a surface changes with a sensitivity which is much better than that, for instance, of the measurement of the electron work function*. However, its relevance to

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* Work functions can be known with an accuracy of ± 50 meV for single crystal faces of metals,[20] while the pzc can be measured with an accuracy of ± 10 mV (or 0.2 pH units).[21]

electrocatalysis must of course be proved. This is straightforward in the case of electrocatalysis for O_2 evolution. Intermediates are in fact oxygenated species (*i. e.* OH groups) bonded to active sites.[22] Since the electrocatalytic activity depends on the strength of the M-OH interaction as the value of pzc does,[11,23] the interrelationship between the two fields is easily established. If the pzc for a set of samples of the same oxide varies, we can expect that also the electrocatalytic activity changes, and *vice versa.*

Fractional Reaction Orders

The fact that the acid-base properties of an oxide surface influence the electrochemical kinetic parameters is proved by the fractional reaction order (*ca.* — 1.5 with respect to H^+) generally observed for O_2 evolution on oxides.[24,25] This reaction takes place with a Tafel slope *b* equal to 40 mV. Electrochemical kinetics tells us that this value is the fingerprint of a mechanism where the second electron transfer is rate determining. The probable steps are the following (S is a surface active site):[19]

$$S + H_2O \leftrightarrow S{-}OH + H^+ + e^- \qquad (6a)$$

$$S{-}OH \rightarrow S{-}O + H^+ + e^- \qquad (6b)$$

$$2S{-}O \rightarrow O_2 \qquad (6c)$$

If step (6b) is rate determining:

$$j \sim [OH] \exp\,[\alpha F\ (E - \Phi^*)\,/\,RT] \qquad (7)$$

where φ^* is the electric potential at the reaction site. Since this is precisely the site where an OH group is adsorbed (Figure 13), the local potential changes with pH as a consequence of reactions (5) according to:

$$\varphi^* \sim (RT/F)\ \ln\ [H^+] \qquad (8)$$

Since step (6a) is in quasi-equilibrium:

$$[OH] \sim [H^+]^{-1} \exp\ [FE/RT] \qquad (9)$$

Substitution of eqn. (9) in eqn. (7) gives finally:

$$j \sim [H^+]^{-(1+\alpha)} \exp\ [(1 + \alpha)\,FE/RT] \qquad (10)$$

Since very often $\alpha \cong 0.5$, eqn. (10) show that a reaction order of — 1.5 is obtained as a consequence of the acid-base dissociation behaviour of the surface sites.

Pzc and Electrocatalysis

The available experimental data point out that the above ideas are sound. Anodic oxygen evolution lends itself especially well to evaluate the electrocatalytic properties of materials since this reaction is a very demanding one and its kinetics is sensitive to the smallest variation in the surface properties of electrodes.[6,22] Samples of RuO_x prepared by thermal decomposition at different temperature show a pzc varying between 4 and 6.[26] Contextually, the Tafel slope *b* for O_2 evolution changes with the calcination temperature and the ln q^* *vs.* ln j plot is nonlinear.[27] All these data suggests that the surface of RuO_x is chemically and physically different at different calcination temperatures.

The situation is radically different for Co_3O_4. Both b and the pzc do not show any detectable variation with the calcination temperature.[28] At the same time *ln* q^* is linearly related to ln j with a unit slope. These results indicate that the chemical nature of Co_3O_4 does not change with the calcination temperature although the extension of the surface area, *i. e.* its physical nature, does.

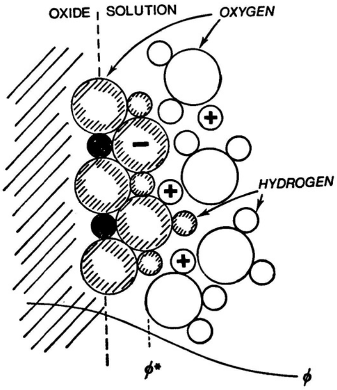

Figure 13. Sketch illustrating the main features of an oxide/solution interface. A negative charged surface site resulting from acid dissociation is shown. The plane of oxygen atoms adsorbed at metal sites is taken as the reacting plane in the case of oxygen evolution. φ^* is the electric potential at the reacting plane.

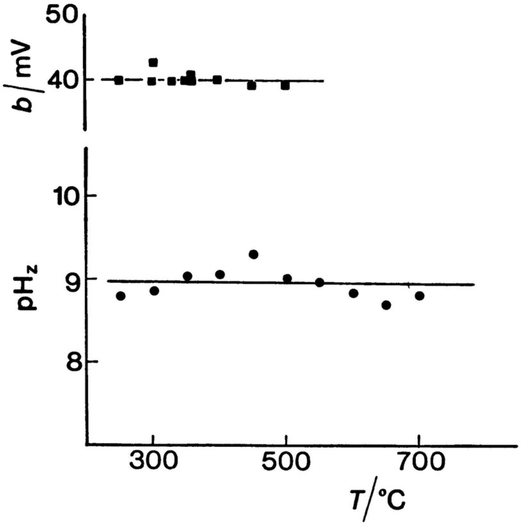

Figure 14. Dependence of the point of zero charge (pH_z) and of the Tafel slope b for oxygen evolution on the temperature of $NiCo_2O_4$ preparation by thermal decomposition of the corresponding nitrates.

Similar results are obtained with another spinel, $NiCo_2O_4$. In particular, Figure 14 shows that the Tafel slope b does not vary with the temperature of calcination as the pzc does not vary over the same temperature range. At the same time the electrocatalytic actvity depends linearly on q^* with a one-to-one correspondence. This suggest that also for $NiCo_2O_4$ the chemical nature of the surface does not depend on the calcination temperature. This (like for Co_3O_4) can be explained in terms of rapid adsorption-desorption of oxygen from the gas phase which results in a calcination independent surface stoichiometry[29] despite a calcination dependent bulk stoichiometry as proved by x-ray and TGA measurements.[8]

CONCLUSIONS

The introduction of oxide electrodes into the electrochemical industry has spurred investigations and approaches which have emphasized the interdisciplinary nature of electrochemistry. Concepts and tools of solid state chemistry and physics, and surface chemistry and physics are all involved in the characterization of oxide electrode surfaces and of their electrocatalytic properties. In particular, this paper has shown that experimental and concenptual approaches more typical of surface (and colloid) chemistry can be extended to the electrochemical field for the evaluation of the catalytic properties of electrode materials.

The available data enable a correspondence between the variation of the acid-base properties and the variation of the catalytic properties to be established for a given oxide obtained by thermal methods with variable composition. The possibility of using the same approach to establish a correlation between acid-base and catalytic properties of different materials, capable of providing a broader predictive basis for the design of electrocatalysts, is still to be proved.

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SAŽETAK

Površinska kemija oksida i elektrokataliza

S. Trasatti

Rad ukazuje na interdisciplinarni karakter istraživanja u području priprave, te fizičko-kemijske i elektrokemijske karakterizacije oksidnih elektroda. Za razumijevanje činilaca koji određuju elektrokatalitičku aktivnost oksida potrebno je razdvojiti geometrijske od elektroničkih parametara. Ukazuje se da je kvaliteta informacije, koja se dobiva *in situ* cikličkom voltametrijom jednaka onoj dobivenoj fotoelektronskom spektroskopijom, dobivenom *ex situ*. Podaci koji se dobivaju idu u prilog tumačenju elektrokatalitičkih svojstava kao acido — baznih disocijacijskih svojstava. Paralelna analiza elektrokatalitičke aktivnosti za razvijanje kisika, i točke nultog naboja ukazuje da se ovaj parametar može upotrebiti kao diagnostički, intenzivni indikator za relativnu elektropatalitičku aktivnost niza oksida. U radu su pokazani podaci za RuO_2, IrO_x, Co_3O_4 i $NiCo_2O_4$.