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The Electrocatalytic Activity of Some Transition Metal Orthosilicates

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After pretreatment with hydrogen at elevated temperatures, some transition metal orthosilicates are electrocatalytically active with respect to the oxygen evolution reaction in alkaline solution. Current–voltage data are given for the Co and Fe orthosilicates. The former appear to be stable at anodic potentials. However, the Fe_2SiO_4 corrodes, which appears to restrict its usefulness as a catalytically active material for this reaction. The compounds showed no significant activity for other electrochemical reactions, for example, hydrogen evolution or oxygen reduction.

There is an urgent and continuing drive to discover new electrocatalysts, for a wide variety of possible applications. This stems partly from purely economic factors, and partly because the catalytic activity of metals and alloys for most electrochemical reactions is either already known or predictable. In the last few years, most such novel electrocatalysts have been of the type $M_1O_x \cdot M_2O_y$ where M_1 and M_2 are usually transition metals, and x and y can be fractional. Outside this category, however, there are very few examples of nonmetallic electrocatalysts, and even fewer still which are active or useful in the more anodic potential regions.

For these reasons, the discovery of electrocatalytic activity in any other class of nonmetallic compound is of some considerable interest. When such a compound is one known also to be a useful gas-phase catalyst, the fact assumes still further interest in view of the ongoing search for similarities and dissimilarities between the two fields of heterogeneous and electrochemical catalysis.

It has long been known that metal–silicon alloys are effective electrocatalysts (*1, 2*) though in the light of reports (*3–6*) that, under a wide range of oxidizing conditions, a thin layer of silica is formed at their surface, this compound generally being considered to be an insulator, the manner in which they functioned was never explained.

Using X-ray diffraction methods, it was shown (*7*) that in addition to SiO_2, species such as Co_2SiO_4 were present in these surface layers and knowing (see below) that this species was a semiconductor, a "cermet" model electrocatalyst was postulated in which the silica film was rendered both conductive and electrocatalytically active as a result of the Co_2SiO_4 particles. It was decided to test this hypothesis by preparing Co_2SiO_4 and fabricating an electrode incorporating this material, extending the work also to the analogous iron and nickel orthosilicates. The results presented here are intended to show, without constituting an exhaustive study, that the transition metal orthosilicates studied do indeed constitute a novel category of nonmetallic electrocatalyst, although a fuller investigation of their properties awaits a more detailed investigation.

Cobalt orthosilicate is a blue–violet crystalline solid with an olivine structure, and is a semiconductor. It is paramagnetic (*8*) at room temperature, and is usually prepared by solid-state sintering of silica with cobalt oxide (*8–10*), though other methods have also been reported (*11–13*). It is worth noting that the ASTM index reports two com-

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pounds with this formula and name (Card 15-865 and 15-497) and in addition, there are a range of cobalt silicate hydroxides such as $Co_3Si_4O_{10}(OH)_2$ (15-387), $Co_3(OH)_2(Si_2O_5)_2$ (21-871), and $Co_3(OH)_4(Si_2O_5)$ (21-872)

Nickel orthosilicate is a green crystalline solid, again with the olivine structure at ambient conditions (*8, 14, 15*), although at higher temperatures and pressures it converts to the spinel form (*16, 17*) At room temperature, it is paramagnetic (*8*) and is a semiconductor (*9*) Its preparation follows that of the cobalt compound Finally, iron silicate is described (*8*) as a brown–green crystalline solid, paramagnetic at room temperature (*8*) and a semiconductor (*18*) It is prepared as the other silicates described below (*19*)

EXPERIMENTAL

(*i*) *Preparation* In this work, three methods were tried for preparation of the transition metal silicates, viz (i) Solid-state sintering, (ii) precipitation from a sodium silicate solution, and (iii) gelling from the tetraethyl orthosilicate (*12*)

However, only the first of these methods was found to give good results and all subsequent studies were based on this route Nickel nitrate, cobalt nitrate, or iron oxalate (BDH "AnalaR" grade), respectively, were intimately mixed with the stoichiometric amount of silica and ground in a pestle and mortar The mixture was transferred to an evaporating basin and gently heated, to allow the salts to dissolve in their own water of crystallization They were then vigorously heated in a crucible to a dull red heat for 30 min, to dry the mixture and decompose the salts to their oxides The resulting mass was reground and heated for 24 h at 1000°C Finally, the mass was ground once more and washed with 5 *M* KOH, then HNO_3 (conc) to remove unreacted silica or metal oxides, respectively After washing with distilled water, it was dried, ground once more, and sealed up for characterization or catalyst fabrication

(*ii*) *Characterization* All samples were characterized by X-ray analysis, powder resistivity and single point BET surface area measurements

X-Ray data were obtained using a Mo target and the results were compared with the ASTM data cards Co_2SiO_4 (15-387, 15-497, 15-865, 21-871, 21-872), Ni_2SiO_4 (3-780), and Fe_2SiO_4 (9-307, 9-484, 11-262, 12-284)

Electrical conductivity was studied using a p t f e conductivity cell with brass end caps The cell was held in a vice and resistance measured using a high impedance voltmeter As prepared, samples showed a relatively low conductivity, of the order of 2×10^{-6} ohm^{-1} cm^{-1} or less, which would have rendered them useless as electrocatalysts In order to improve their conductivity they were heated, initially in argon (without effect) and subsequently in H_2 at 800°C for 2 h which led to an increase in conductivity (for the cobalt species) to 6×10^{-2} ohm^{-1} cm^{-1} The BET surface area of all samples was of the order of 20 m^2/g X-Ray data showed that such treatment did not cause reduction of the silicate to any significant extent However, mindful of the literature on the subject (*20, 21*), it was clear that extension of this treatment could lead to reduction The same treatment applied to the other two silicates resulted in complete reduction of the Ni silicate to the metal and silica, and a partial reduction of iron silicate in the same way The possibility of using less extreme conditions to avoid this remains for future investigations of these compounds

(*iii*) *Electrode preparation* Electrodes were fabricated by application of a mixture of the catalyst, p t f e dispersion (I C I G51 Dispersion) and water, previously mixed in an ultrasonic bath, onto a 1-cm square wire mesh Ni meshes were used for trials in alkaline media, Pt in acid media After application, with a paintbrush, the solvent was evaporated off using a hot-air blower, and the electrodes were cured for 1 h at 300°C The initial p t f e catalyst ratio of 10 3 proved too hydrophobic and was replaced by one of 10 1 ratio

(*iv*) *Electrochemical testing* The catalysts were tested under potentiostatic conditions in a standard three-compartment cell, using a Chemical Electronics 40-3A potentiostat A large Pt screen counterelectrode was used The reference electrode was a dynamic hydrogen type except in NaCl where a saturated calomel type was used For gas evolution studies, the electrode was immersed close to the Luggin capillary For oxygen reduction studies, a floating electrode (i e , positioned horizontally at the electrolyte–gas interface) mode was used In this way, steady-state current–voltage data were obtained for the different catalysts, for oxygen evolution and reduction, as well as hydrogen and chlorine evolution In cases where results seemed promising, long-term tests were carried out at a fixed potential, to test the stability of the catalyst

Currents shown are "gross," that is to say including an element from the supporting metal screen However, the magnitude of this contribution has been determined in previous work (*22*) and this knowledge allowed an assessment of that contribution to be made

RESULTS

Before consideration of the results in detail, the following points must be made In the first place, the electrocatalysts were prepared on a very small scale, and to this extent, minor variations from batch to batch of catalyst morphology, or catalyst loading on the supporting screens, were unavoidable Second, it must be recognized that these electrodes, as made, are complex structures which undergo a number of changes, both physical and chemical, in the initial period of their life Thus the initial application of anodic potential caused changes in the wettability of the various regions of the catalyst surface, and some material was lost which could cause both increase and decrease of true surface area These are some of the factors underlying the complex behavior shown in the long term tests to be described below For the same reason, quite apart from potential-time "life tests," electrodes were only subjected to measurements after an initial "preanodization" period at a potential (2 000 V vs DHE) much higher than that encountered during the actual tests reported here

The corrosion of the catalysts is also considered below and it is emphasized that this is defined here in terms of detectable metal ions in solution (more than 2 ppm) What was not systematically studied (although the phenomenon was observed) was the loss, probably associated with alkaline dissolution of siliceous materials, of particulate matter, most probably Co_3O_4, which does not dissolve in alkali and would thus not be detected using atomic absorption

(*i*) *Cobalt Silicate*

Steady-state oxygen evolution data in 5 *M* KOH at several temperatures are shown in Fig 1 The data are iR-corrected, using an interrupter technique (*23*)

Preanodization appeared to make the electrode surface more hydrophilic, and to accelerate the achievement of the quasi steady state Because the rates for O_2 evolution on Co_2SiO_4 appeared as good as other similar catalysts, long-term tests were run, at 40°C and 1 A cm^{-2} These tests were suspended over weekends and at nights as the cell required continual topping up with water to replace losses due to spray and evaporation The results of one such test (again iR-corrected) are shown in Fig 2

Other experiments with cobalt silicate are summarized in Table 1

(*ii*) *Iron Silicate*

Oxygen evolution runs on this catalyst were accompanied by formation of a pinkish tinge in the solution around it and atomic absorption analysis of the solution

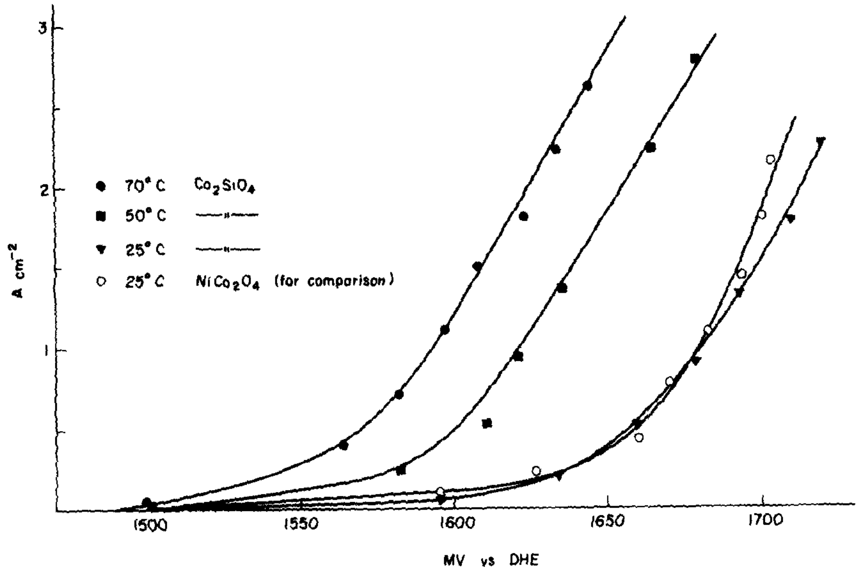

FIG 1 Polarization plots for Co_2SiO_4 at three temperatures, 5 *M* KOH Plots are corrected for ohmic drop Data for $NiCo_2O_4$ shown for comparison (from Ref (*22*)) Data obtained after quasi-steady state reached following preanodization

revealed traces of iron present As iron in cationic form would normally form the ferric hydroxide in 5 *M* KOH, this was assumed to be anionic (such as FeO_2^{2-}), and the Pourbaix diagram (*24*) shows this to be the expected species However, on standing, the pink color faded and iron hydroxide was precipitated That this release of iron was due to anodic attack on the orthosilicate and not just to traces of free iron in the

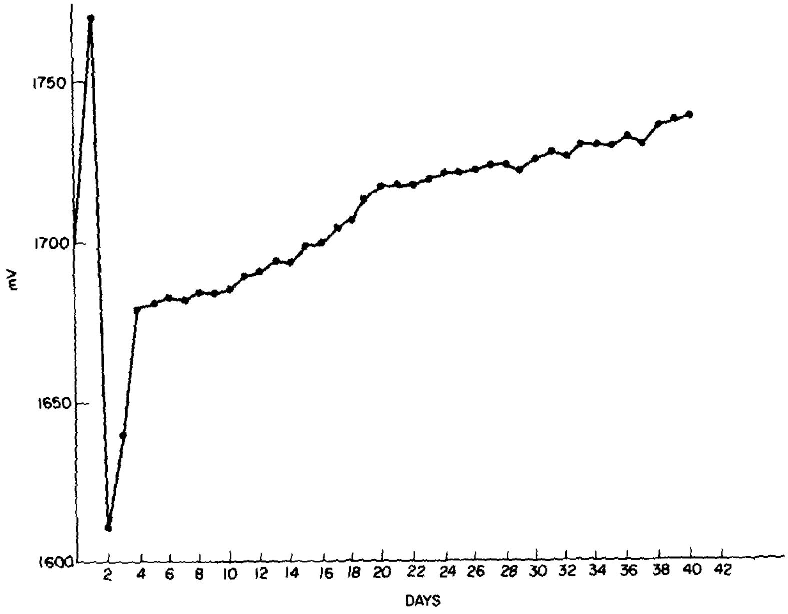

FIG 2 Potential time plot for Co_2SiO_4 electrode (21 mg/cm^2 loading) held at 1 A cm^{-2} in 5 *M* KOH at 40°C

TABLE 1

Compound	Test Reaction	Result	Comments
Ni_2SiO_4		No tests run	Adequate electrical conductivity not achieved
Fe_2SiO_4	O_2 evolution 5 *M* KOH		See Fig 3, Corrosion observed
Co_2SiO_4	H_2 evol 5 *M* KOH	75–100 mA cm^{-2} at −300 mV vs DHE	Activity implies major contribution from screen
Co_2SiO_4	O_2 red 5 *M* KOH	3 mA cm^{-2} at +500 mV vs DHE	Activity implies major contribution from screen
Co_2SiO_4	Cl_2 evol 5 *M* NaCl	100 mA cm^{-2} at 800 mV vs SCE	Visible corrosion
Co_2SiO_4	O_2 evol 5 *M* H_2SO_4	5 mA cm^{-2} 1800 mV vs DHE	Atomic absorption indicated corrosion

catalyst, was confirmed by carrying out weight loss experiments After 168 h at 1 A cm^{-2} the catalyst was found to have lost 6 mg of its original 12 mg loading The current–voltage data before and after this run are shown in Fig 3

DISCUSSION

From our data, it can be seen that the transition metal silicates can be added to the modest list of classes of compounds showing electrocatalytic activity, even though only the cobalt species showed the degree freedom from corrosion which useful catalysts must possess Furthermore, the good activity shown by the cobalt silicate for oxygen evolution (another catalyst is shown in Fig 1 for comparison) appears to be very specific, being restricted to this one reaction, its activity for other reactions being very poor, as shown in Table 1 The iron silicate is similarly limited in its catalytic activity, and this activity is accompanied by corrosion, which appears to render the catalyst of no practical use

The finding that the silicates can show electrocatalytic activity focusses attention on the metal–silicon alloys widely used as anodes The presence of Co_2SiO_4 in the surface layers formed on Co–Si alloys (7)

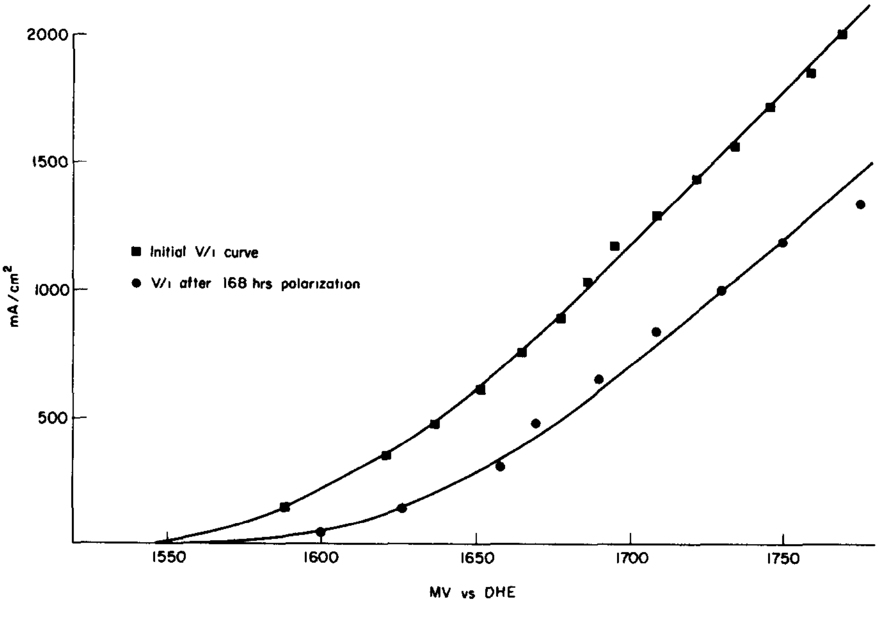

FIG 3 Polarization plot for Fe_2SiO_4 KOH (5 *M*) 25°C Corrected for ohmic drop Upper curve, initial data Lower curve, after 168 h polarization

prompted the present investigation Since that time, however, we have sought without success (*25*) to detect the analogous Fe_2SiO_4 in the surface layers formed on Fe–Si alloys Its absence seems to offer one of two conclusions Either (as suggested by observations in this work) it is present under anodic conditions but is reduced by the time the surface layers are submitted to X-ray analysis Alternatively, it is not present, and the catalytic activity of the Fe–Si anodes is due to an alternative process A clue to the nature of this is provided in a recent paper by Madou and Frese (*26*) who show that doping of silica renders it catalytically active for electrochemical redox reactions For cathodic reactions, the catalytic activity is "permanent" For anodic reactions, the activity decays over a short period of time, as the dopant cation migrates out of the SiO_2 under the potential gradient However, when the SiO_2 is formed above an Fe–Si substrate, which by anodic dissolution is releasing Fe^{2+} cations, a continuous source of these dopant cations is thereby provided The question which therefore remains at the end of this work (and not just in respect of cobalt and iron) is the extent to which one or both of these catalysis mechanisms are important Pt, Pd, Ni, and Mo are only some of the metals (*1, 27*) whose silicon alloys have been shown to display catalytic activity and further work is clearly called for to discover the basis of such activity

The corrosion (anodic dissolution) of the silicates was not a prime target in the present study, and yet, as can be seen, its occurrence constitutes a barrier to their use as catalysts Here it is interesting to note that the cobalt compound is more corrosion resistant than its iron analog, thus following the normal rule for alloys of these metals, where, for example, the Co–Cr alloy is more corrosion resistant than the corresponding (atomic percentage) Ni–Cr alloy (*28*)

Those engaged in the study of electrocatalysis should always be mindful of analogous gas-phase studies What relevant findings have been reported in the present case?

First, it is known that the transition metal silicates are active gas-phase catalysts Reference may be made to the work of Kondrashava (*29*) on Co_2SiO_4 as a catalyst Morikawa (*30*) has studied the Ni silicate and, most interestingly, reports that it possesses little activity until heated for 1 h in H_2 at 500°C One asks whether, in some way, Morikawa managed to obtain his compound in a more conductive form, since as many authors, such as Wolkenstein (*31*) and more recently Kreja (*32*) have shown (the latter in respect of the catalytic activity of cobalt oxide) that a parallelism exists between electrical conductivity and catalytic activity

The nature of the conductivity of this class of compound has formed the subject of some debate Kreja (*32*) suggests that a transition from *p*-type to *n*-type occurs as the temperature increases Bykovskii (*33*), studying the beryllium orthosilicate, suggests that both electronic and ionic conducting processes occur, but once again the temperature and doping history influence these Gottschalck (*34*) has studied the conduction process in Co_2SiO_4 to reach a similar conclusion Thus one opines that the nickel silicate might be made conductive, though there are no reasons to believe its catalytic activity would be superior to that of the cobalt compound, while its corrosion resistance (drawing on the model for these alloys referred to earlier) would be expected to lie between Co and Fe

Whether the catalytic activity, both gas phase and electrochemical, of the cobalt silicate can be related to the finding (*35*) in which glass fibers, fused with cobalt oxides, show catalytic activity, or what relationship there is, if any, between the work of Pope and Walker (*36*) on silica-supported cobalt oxide catalysts, must remain speculative However, when comparisons have been made between gas-phase and electrochemical catalysis (*37*), the many similarities between the two fields have hitherto been marred by the total absence of silica or its derivatives from the electrochemical field Here, for the first time, we have shown that this compound, too, has common importance in both electrochemical and gas-phase catalysis We have no doubt that further studies in the field will reinforce such similarities

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