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EFFECT OF ELECTRIC FIELDS ON THE THERMAL DECOMPOSITION OF CALCIUM CARBONATE

K.J.D. MACKENZIE * and N. HADIPOUR

Materials and Energy Research Centre, Aryamehr University of Technology, Tehran (Iran)

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ABSTRACT

The thermal decomposition of $CaCO_3$ powder and single crystal samples to CaO has been shown by X-ray diffraction and ESCA to be assisted by the application of external DC electric fields during the reaction. The effect is particularly marked at the positive electrode. The results are discussed in terms of both ionic migration effects and the field-induced electro-adsorption/electro-desorption of gaseous CO_2 at the surface of a semiconductor. Approximate calculations based on both theories show that ionic migration cannot account for the magnitude of the observed effects, but a reasonably satisfactory explanation is provided by the application of semi-conductor surface theory to the system.

INTRODUCTION

The thermal decomposition of calcium carbonate is a much-studied solid state reaction, of which the kinetic aspects have received particularly close attention from many workers (see, for example, the bibliography given by Beruto and Searcy [1]). Despite extensive study, discrepancies between the various published results are common, and suggest that the reaction is rather sensitive to factors such as sample geometry and particle size, reaction atmosphere, heating rate, etc.

In addition to its academic interest, the decomposition of calcium carbonate is of practical importance in the lime and Portland cement industries, and during a recent study of the effect of electric fields on the thermal formation of Portland cement clinker [2], some evidence was found that the decomposition of calcite in the reaction mixture is assisted by an applied DC electric field, particularly at the positive electrode. The aim of the present work was to investigate this unexpected effect by making electrolysis studies on the decomposition of pure $CaCO_3$ powder and natural calcite single crystals. It was also hoped that these studies might help to clarify some of the mechanistic details of this important reaction.

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* Present Address: Chemistry Division, D.S.I.R., Private Bag, Petone, New Zealand.

EXPERIMENTAL

The $CaCO_3$ powder used in this work was of analytical reagent grade. The single crystals of natural calcite were hand-picked specimens from Yazd, Kerman province, Iran, kindly supplied by Dr. M. Sadazardeh Yaganeh, Geological Survey of Iran. The trace element analysis of this calcite is shown in Table 1.

The powder electrolyses were carried out on samples compacted into a cell described by MacKenzie [3] in which the lower electrode was a platinum foil and the upper electrode was of platinum mesh, to facilitate the removal of the gaseous product. The filled cell was introduced into a pre-heated tube furnace, allowed to equilibrate and the electrolysing voltage, from a Brandenburg model 475R E.H.T. power supply established across the electrodes. Two sets of experiments were made in ambient air; in one set, the effect of temperature was investigated at a constant field strength and reaction time (4.2×10^4 V m^{-1}, 0.5 h, respectively), and in the other set, the effect of field strength was investigated, at constant temperature and reaction time (850°C, 0.5 h). Each experiment was repeated with the upper electrode at reverse polarity, and a series of control experiments were also made in which no electric field was applied.

At the conclusion of each experiment, the sample was quenched by withdrawing from the furnace, the upper electrode was removed and a small amount of sample was taken from that region for CaO analysis by quantitative X-ray diffraction. The internal standard was rutile, added as 10% by weight. The peaks used for analysis were the 200 CaO peak at $d = 2.405$ Å and the 110 rutile peak at $d = 3.25$ Å. The intensities of these peaks were measured by cutting them out of the X-ray chart and weighing, and the method was calibrated against pure CaO, prepared by thermally decomposing the carbonate. The reproducibility of the analytical method was found to be better than 5% (in most cases about 3%).

Electrolysis experiments were carried out on the single crystal calcite samples by grinding and polishing the electrode faces flat and parallel and vacuum depositing a thin film of platinum to ensure good electrical contact. The cell in which these experiments were carried out has been described previously [4]. After electrolysis at 750°C for 4.5 h, the samples were with-

TABLE 1

Trace-element content of natural calcite crystals determined by semi-quantitative DC arc spectroscopy

Element	%
Mn	0.08
Sn	0.01
Mg	0.005
Si	<0.01
Al	<0.01

drawn from the furnace and cooled, still under the influence of the electric field. The samples were then examined by Scanning Auger spectroscopy and ESCA, in a Physical Electronics Combined Auger/ESCA/SIMS spectrometer. Particular attention was paid to the areas of the sample immediately adjacent to the electrodes.

RESULTS AND DISCUSSION

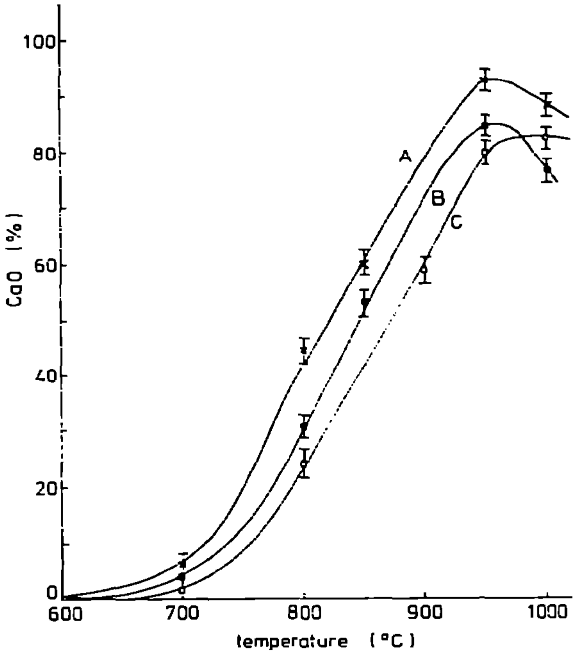
Electrolysis experiments on compacted powders

The results of these experiments at various temperatures are shown in Fig. 1, and the results of the field-strength dependence experiments are shown in Fig. 2.

Several points emerge from Figs. 1 and 2:

(i) Under all conditions, the degree of decomposition of the carbonate to the oxide is significantly greater at the positive electrode.

(ii) The degree of reaction displays an expected increase with increasing temperature, both in the presence and absence of electric fields. However, at the highest temperature (1000°C), this effect is diminished, particularly in the electrolysed samples, in which the reaction is actually retarded, especially at the negative electrode. One possible explanation is that at the



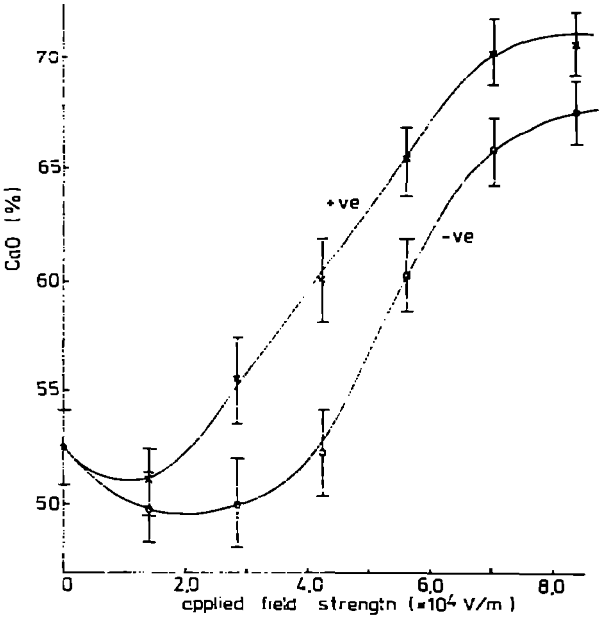


Fig. 1. Temperature dependence of the decomposition of $CaCO_3$ powder under electric fields. A, positive electrode; B, negative electrode; C, unelectrolysed. Reaction time 0.5 h, applied field strength 4.2×10^4 V m^{-1}.

Fig. 2. Field-strength dependence of the decomposition of $CaCO_3$ powder. Reaction time 0.5 h, temperature 850°C.

highest temperature, the escape of gaseous products ceases to be limited by the kinetics of the decomposition process and becomes limited by the cell geometry. The apparent retardation at the negative electrode may be due to additional retention of the gaseous product at that electrode as a result of an electro-adsorption effect which will be discussed in detail later.

(iii) The degree of reaction increases regularly with field strength, but the effect tails off at the highest field strength used here, possibly due to some saturation effect. Higher field strengths could not be used because of limitations in the current available from the power supply (7 mA) and the tendency for arcing to occur between the electrodes at higher field strengths.

The disparity between the degree of reaction at the negative and positive electrodes under all conditions suggests that some polarization effect is occurring. This could be the result either of ionic transport within the samples, or of some surface phenomenon at the gas—solid interface in the region of the electrodes.

Although in the case of the thermal decomposition of metal hydroxides under electric fields, the reaction appears to involve proton migration to the cathode, followed by the discharge of water in that region [5—7], a similar process is difficult to envisage in carbonate decomposition, since the gaseous product is electrically neutral, and no small, mobile species appear to be involved in the reaction. However, information about possible ionic movements can be inferred from the temperature dependence of the electrical conductance of calcium carbonate. DC measurements reported by Hashimoto [8] for single crystals and powder compacts of $CaCO_3$ show that the pre-exponential factor of the temperature dependence equation above about 400°C is 300—400 times greater for powder compacts than for single crystals. This was explained in terms of enhanced ionic mobility along the grain boundaries of the polycrystalline compacts, but no evidence is presented by Hashimoto regarding the nature of these ions. Again, the marked decrease in the measured current with time observed by Hashimoto [8] may be evidence of polarization, and a "blocking" effect of ions migrating to one or other electrode region. The activation energy reported for the conductance process by Hashimoto [8] was 146.5 kJ mole^{-1} for single crystals and both coarse and fine powder compacts. This conductance activation energy is similar to that reported for CaO (146.5—167 kJ mole^{-1} [9], 145 kJ mole^{-1} [4]); the similarity between these values and the activation energy for Ca self-diffusion in CaO [10] suggests that the migrating ions in both CaO and $CaCO_3$ are Ca^{2+}. The relationship between Ca^{2+} diffusion and ionic migration under the influence of electric fields is also apparent in studies by Arnikar and Chaure [11], who have shown that the diffusion coefficient of Ca^{2+} in $CaCO_3$ is increased by the application of external electric fields of the approximate strength of those used here, especially in the direction of the field (at 300°C and a field strength of 1×10^4 V m^{-1}, the diffusion coefficients were reported as 6.3×10^{-11} cm^2 sec^{-1} in the field direction and 5.1×10^{-11} cm^2 sec^{-1} against the field direction, compared with 4.9×10^{-11} cm^2 sec^{-1} in the absence of the field). An alternative possibility, of carbonate (or oxide) ion migration should not be overlooked, but self-diffusion data for carbon and oxygen in calcite [12] indicate that the activation energy for carbon diffusion at 250—550°C (71 kJ $mole^{-1}$) is much lower than the reported conductance activation energy in calcite; the migration of a carbon-bearing ion or oxyanion does not appear likely to be involved in the present electrolysis process.

If it is accepted that some Ca^{2+} migration occurs under the influence of DC electric fields, the question remains as to its possible effect on the decomposition of the carbonate. Polarization of calcium towards the negative electrode would result in the depletion of this species from the positive electrode region with consequent destabilization and eventual dissociation of the carbonate ions in that region. A rough calculation can be made to see whether this would account for the degree of increased decomposition observed under electrolysis. Let us assume (i) an estimate of the maximum number of calcium ions which could be displaced from their lattice positions is given by Faraday's Laws, even though these ions may not in fact be discharged at the cathode as the metal, (ii) for each cation thus displaced, one carbonate ion is dissociated, and (iii) the effect of this electrolysis is additively combined with the normal thermal dissociation under the same conditions. For the case of electrolysis of 850°C for 1800 sec and 7.0×10^4 V m^{-1} (Fig. 2), the current flowing (calculated from the resistance of the sample measured at that temperature using a Wayne-Kerr model B642 bridge) is 2.0×10^{-4} A. Then, by Faraday's Laws, the quantity of Ca^{2+} displaced is related to the current I, time t, equivalent weight W and valency n by:

$$Q = (ItW)/nf \qquad (1)$$

where F is the Faraday (≈96,500 coulombs).

Thus, 7.48×10^{-5} g Ca should be displaced by the present current. This corresponds to the decomposition of 1.87×10^{-4} g $CaCO_3$ and the formation of 1.05×10^{-4} g CaO. From Fig. 2, the normal thermal processes in unelectrolysed samples at this temperature and time lead to the formation of 52.5% by weight of CaO, or, based on the weight of cell packing for a typical experiment, a mixture of 0.439 g CaO and 0.397 g $CaCO_3$. Thus, the maximum effect of the electrolysis process, as calculated from Faraday's Laws in terms of an increase in percentage of CaO, would not be experimentally detectable if the effect is assumed to be integrated throughout the sample bulk. Even if the effect is assumed to be confined to the immediate region of Ca depletion (the anode region), the experimental results cannot be accounted for, since significantly increased decomposition is observed in both the cathode and anode regions (66.5 and 71.0% CaO, respectively).

The second possibility, that some electrically induced surface effect causes retention or desorption of the gaseous product, can be treated in terms of current semiconductor theory. When a semiconductor is subjected to an electric field, the surface potential changes, and the resulting injection or removal of electrons causes a bending of the valence and conduction bands. Gaseous species may then be adsorbed in the vicinity of an electron or hole at the semiconductor surface, the bonds thus formed being of increased strength. In electric fields of positive polarity, de-electronation occurs and the Fermi level is lowered; this condition leads to increased desorption of electron-accepting gaseous molecules (or increased adsorption of electron-donating molecules). The reverse is the case at negatively-charged semiconductor surfaces. This effect has been verified for the interaction of CO_2 with p-type tellurium [13] in which electro-adsorption was found to be enhanced on negatively-charged surfaces. A similar effect could be envisaged with CaO, which is a p-type semiconductor at elevated temperatures and atmospheric oxygen pressure [9]. Such an effect would qualitatively explain the presently observed results, since by analogy with tellurium, the field should cause increased retention of the gaseous reaction product at the negative electrode and increased desorption at the positive electrode; the degree of decomposition should therefore be greater at the positive electrode than at the negative, which is consistent with the present findings.

An estimate of the probable magnitude of this effect can be made, since the fraction η^- of gaseous molecules which form stable bonds with the charged semiconductor surface is given by Ivankiv and Muzychuk [4] as:

$$\eta^- = \{1 + \exp[(f^- - f^0 - F_0 - e\phi)/kT]\}^{-1} \quad (2)$$

where f^- and f^0 are the free energies of the tightly-bound and normally-bound adsorbed species respectively, F_0 is the Fermi level of the semi-conductor in the absence of the field and ϕ is the displacement of the edge of the semiconductor bands due to the field. A precise evaluation of ϕ is very difficult, but, following Ivankiv and Muzychuk [14], a crude approximation can be made by taking into account only the direct effects of the applied field. The band bending is then approximately given by:

$\phi = E_s L$ (3)
where $E_s = [2kT/\epsilon\epsilon_0]\,[n^0(e^y - 1) - N_d y]^{1/2}$ (4)
and the Debye length $L = (\epsilon\epsilon_0 kT/e^2 n^0)^{1/2}$ (5)
and $y = eE_0 L/kT$ (6)

where n^0 is the equilibrium concentration of charge carriers in the electrically neutral bulk of the semiconductor, N_d is the concentration of donors (likely to be very small in the present samples), ϵ and ϵ_0 are the dielectric constants of the semiconductor and of free space respectively and E_0 is the applied field strength. These equations are in SI units, unlike those of the original reference. We shall now calculate the dependence of η^- on field strength for CaO at 850° C. At this temperature, the electronic population of the conduction band can be calculated to be similar to that of a semiconductor having a bandgap of 2.6 eV at room temperature. Then,

$$n^0 = [N_c N_v \exp - (e_c - e_v)/kT]^{1/2} \quad (7)$$

where $(e_c - e_v)$ is the bandgap, and the effective density of states $N_c = N_v \approx 10^{25}\ m^{-3}$. A value of $1.5 \times 10^{19}\ m^{-3}$ is thus calculated for n^0. Taking a value of 7.8 as the mean dielectric constant for CaO [15], a value of 1.68×10^{-6} m is estimated for L. (This is of the expected order of magnitude for the Debye length in normal semiconductors.) Values of y and E_s at various field strengths are now calculated, assuming $N_d \approx 0.0001\%\ n^0$ (E_s turns out to be very insensitive to the assumed value of N_d). To complete the calculation of η^-, values of f^- and f^0 were taken to be of the same order of magnitude as the respective free energies of chemisorption and physical adsorption, typically 12—18 eV and 0.01—0.2 eV [16]. Taking f^- as 5 eV, f^0 as 0.015 eV and F_0 as 1.3 eV, the field strength dependence of η^- thus calculated is shown in Fig. 3.

The shape of the calculated curve is formally similar to the field-strength dependence of the degree of decomposition (Fig. 2), although on the basis of the present assumptions the theoretically predicted onset field strength is somewhat higher than in Fig. 2, and the calculated range of field strengths over which the effect operates is rather narrower than observed in the present experiments.

Figure 2 shows that at 850°C and a field strength of 7.0×10^4 V m^{-1} 18.5% more CaO is formed at the positive electrode than in the unelectrolysed control under the same conditions. Allowing for the fact that the sample weight is reduced by the loss of gaseous product, the additional weight of $CaCO_3$ decomposed in the electrolysed sample amounts to 0.178 g, corresponding to 1.78×10^{-3} moles of CO_2 evolved. Since the unelectrolysed control contains a total of 1.18×10^{-2} moles, the fraction of carbonate ions additionally dissociated in the electrolysed sample is 0.151. If it is assumed

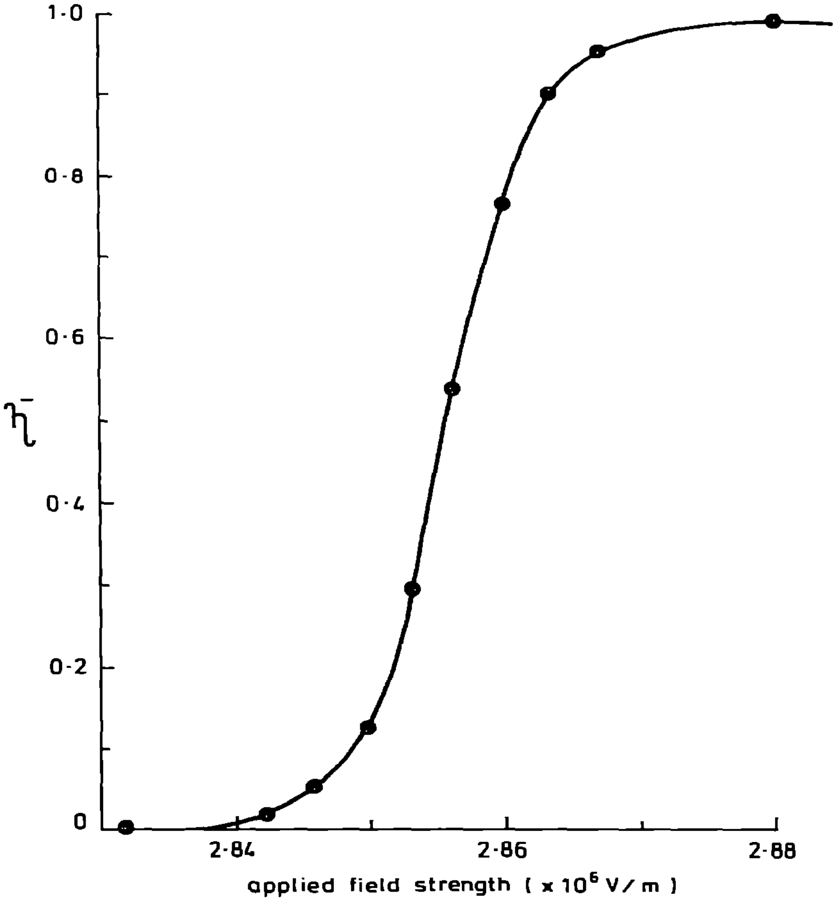


Fig. 3. Calculated field strength dependence of η^-, the fraction of stable bonds formed between gaseous molecules and a charged CaO semiconductor surface at 850°C.

that each CO_2 molecule desorbed from the positive electrode region represents an additional molecule of $CaCO_3$ dissociated, this fraction can then be directly equated with η^-. From Fig. 3 it can be seen that η^- has a value of 0.151 at a field strength of about 2.86×10^6 V m^{-1}, in quite reasonable agreement with the actual field strength used, bearing in mind the approximate nature of the calculations. Thus it appears that such an electro-adsorption—desorption mechanism could account for the magnitude of the observed effect.

The observation that decomposition is also enhanced, but to a lesser extent, at the negative electrode requires comment, since the foregoing theory suggests that the reaction should be retarded at this electrode by comparison with the unelectrolysed control. This discrepancy is possibly related to the fact that the observed effect is not a simple adsorption/desorption phenomenon, but is a chemical decomposition, in which co-operative processes occur in the bulk of the sample as well as at the electrodes. Further, since the material is polycrystalline, polarization could occur in each individual crystallite throughout the bulk, leading to effects which would not be predicted by theory developed for monocrystalline samples.

Electrolysis experiments on single crystals

In these experiments, an attempt was made to distinguish small differences in the concentration of physical and chemical state of the material in the two electrode regions using surface analysis techniques. Scanning Auger spectroscopy revealed no detectable differences in the state of the calcium, carbon or oxygen in the electrolysed and unelectrolysed samples, although differences in the relative intensities of the various peaks were noted. The intensity measurements appear to suggest that a higher carbon concentration occurs in the negative electrode region than in the positive, in agreement with the X-ray findings of higher carbonate concentrations in that region. However, measurements of the oxygen/calcium intensity ratios suggest a relatively higher oxygen concentration at the *positive* electrode face, which would not be expected from the X-ray results; this illustrates the need for caution in attempting to extract quantitative information from Scanning Auger measurements, particularly in systems such as this, in which some elemental lines overlap.

Clearer differences were observed in the ESCA spectra of the electrolysed and unelectrolysed samples. The intensity ratio of the 1*s* oxygen peak to the 2*p* calcium peak was significantly greater in the negative electrode material than in the positive, where the ratio was very similar to that found in pure CaO powder. This result is consistent with a higher concentration of $CaCO_3$ at the negative face. Even more striking differences were recorded in the binding energies of Ca(2*p*) (Fig. 4) and O(1*s*) (Fig. 5).

In these diagrams, the values of the binding energies are referred to that of the 1*s* carbon peak which occurred in all the spectra, and for which a binding energy of 285.0 eV was assumed. Figures 4 and 5 show that small but measurable differences exist in the binding energies of Ca and O in oxide and carbonate matrices. Comparison of the spectra of the negative and positive elec-

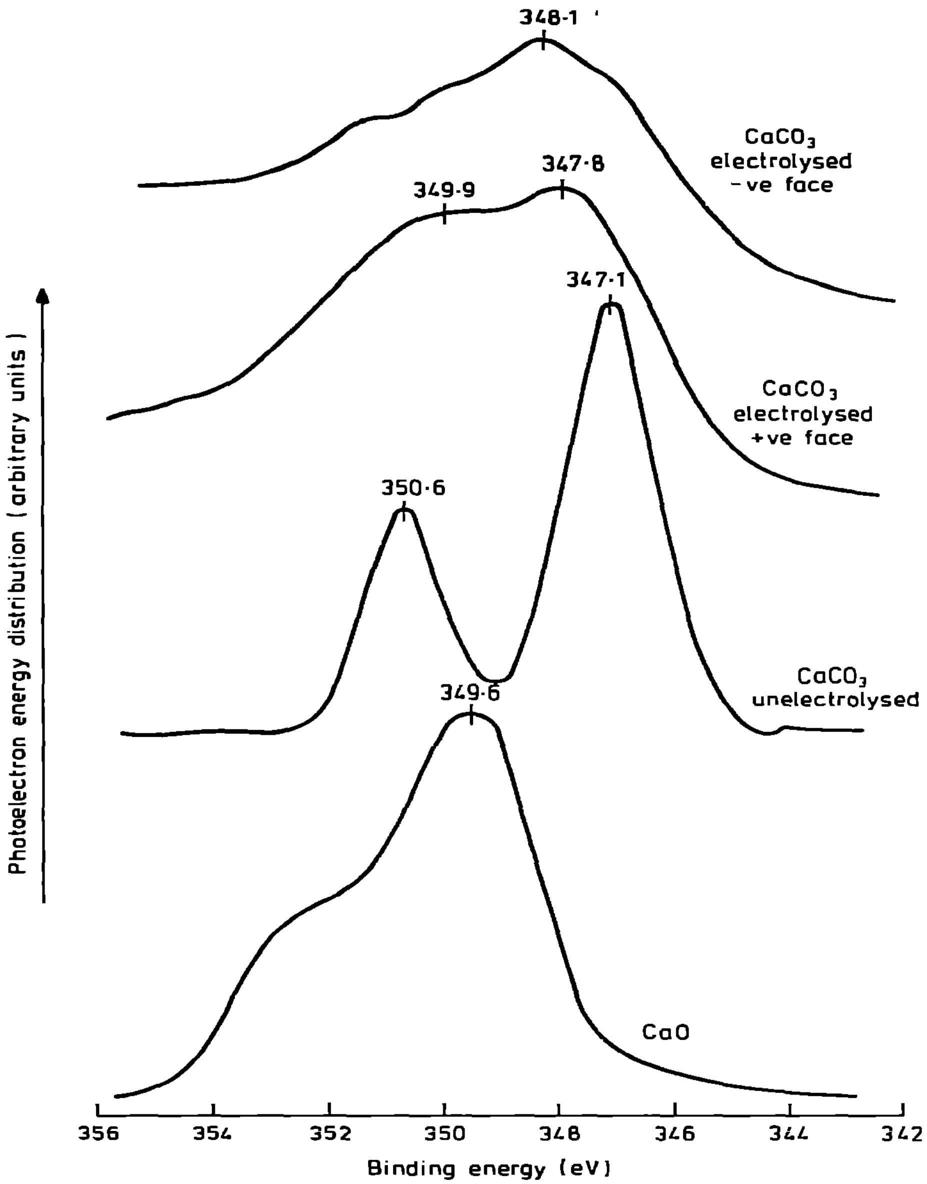


Fig. 4. Typical calcium ESCA spectra of electrolysed and unelectrolysed $CaCO_3$ single crystals and pure CaO powder. Excitation source: Mg anode. Binding energies are relative to the 1*s* carbon peak at 285.0 eV.

trode regions of an electrolysed sample with those of an undecomposed carbonate single crystal and a pure oxide powder suggests that the concentration of carbonate is higher in the negative face than in the positive, again consistent with the X-ray results on polycrystalline powders.

CONCLUSIONS

The thermal decomposition of calcium carbonate powder to the oxide is assisted by externally applied electric fields, particularly at the positive elec-

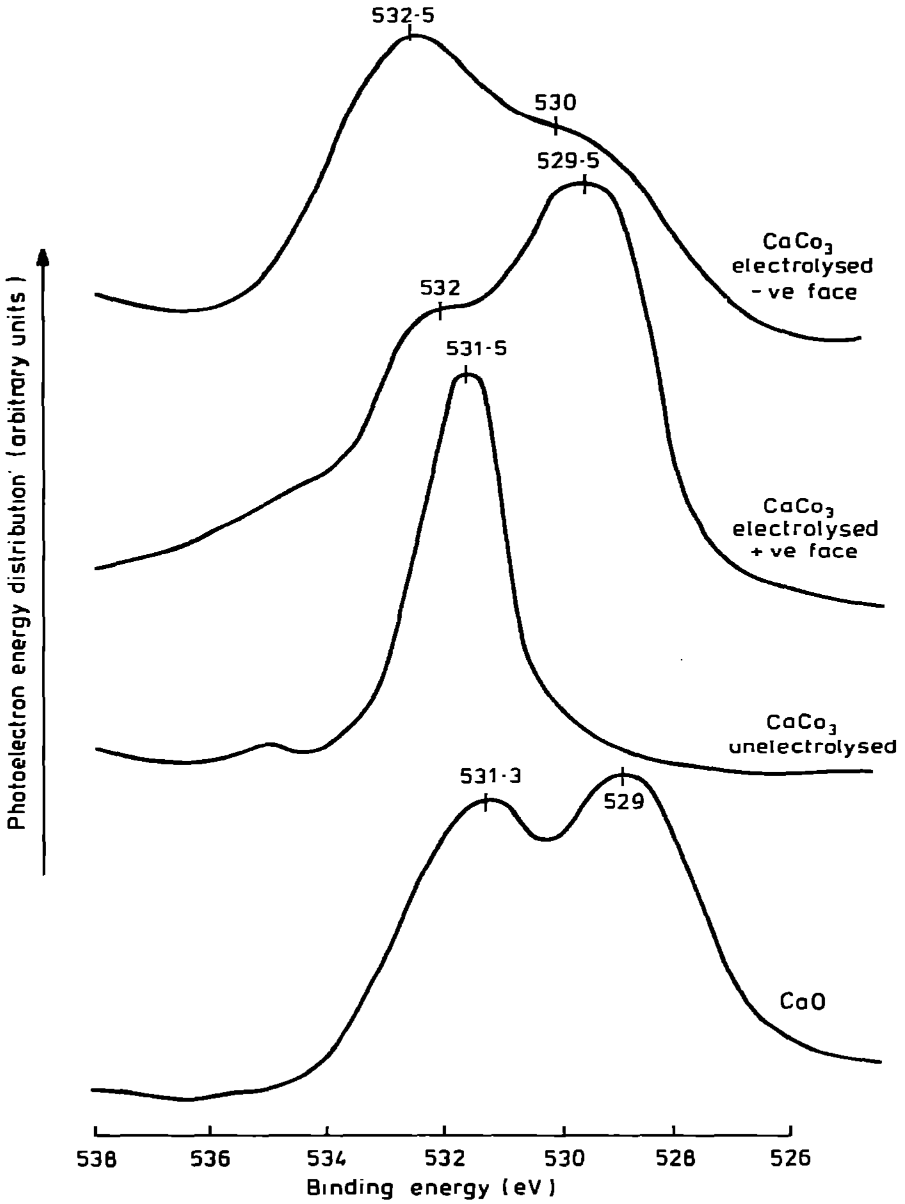


Fig. 5. Typical 1*s* oxygen ESCA spectra of electrolysed and unelectrolysed $CaCO_3$ single crystals and pure CaO powder. Excitation source: Mg anode. Binding energies are relative to the 1*s* carbon peak at 285.0 eV.

trode, over a range of field strengths and reaction temperatures. This effect was also demonstrated in electrolysed single crystal sample by Scanning Auger spectroscopy and ESCA.

Although migration of Ca^{2+} probably occurs in these samples, crude Faraday's Law calculations suggest that the observed effect of the field is too great to be explained solely in terms of cationic migration. An alternative mechanism, involving electro-adsorption or electro-desorption of gaseous CO_2 at the surface of a semiconducting oxide, provides a qualitative explanation of the observed effect, and an approximate calculation of the magnitude of the effect suggests that it could account for the results.

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