Surface modification of RuO$_2$ electrodes by laser irradiation and ion implantation: Evidence of electrocatalytic effects[†]

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Abstract.   RuO$_2$ thin layers were deposited on Ti supports by thermal decomposition of RuCl$_3$ at 400°C. Some of the samples were subjected to laser irradiation between 0·5 and 1·5 J cm^{-2}. Some others to Kr bombardment with doses between 10^{15} and 10^{16} cm^{-2}. Modifications introduced by the surface treatments were monitored by cyclic voltammetry and O$_2$ evolution in H$_2$SO$_4$ solution. The voltammetric charge increased with surface treatment almost to the same extent for irradiation and bombardment. The electrocatalytic activity turned out much higher for Kr bombarded samples. Raw experimental data were scrutinized in an attempt to separate geometric from electronic factors. True electrocatalytic effects are clearly seen to prevail over purely surface area effects.

Keywords.   Electrocatalysis; surface modification; laser irradiation and ion irradiation.

1. Introduction

RuO$_2$ became popular in electrochemistry as it was introduced into the technology as the active component of the so-called DSA® (Dimensionally Stable Anodes) for chloro-alkali cells.[1–3] Fundamental research to understand the origins of its activity started in late 60's,[4] expanded exponentially[5] and still arouses much interest in the field of electrocatalysis.[6,7]

The activity of RuO$_2$ has been attributed to both electronic and geometric effects. The latter are related to the high surface area as a consequence of the procedure of preparation of oxide materials. The former are attributed to the capacity of transition metals to exist in several valency states so that electron exchange with the environment is possible at several different redox potential levels.[8]

Deeper investigations of the properties of RuO$_2$ layer electrodes have shown that electronic and geometric factors are interrelated as the size of the oxide particles decreases. More specifically, as the surface area increases the mechanism of electrode reactions changes as a consequence of the appearance of particularly active sites at the surface of smaller and smaller crystallites.[9]

A definitive proof that particularly active sites form on especially defective surface regions of oxide particles can be obtained if such sites are promoted on the surface of normal-sized crystallites by surface modification with specific treatments. Experiments of irradiaton with γ-rays were carried out several times in catalysis[10,11] and sometimes in electrochemistry.[12] Increase/decrease in catalytic activity was reported depending on specific conditions.

Treatments with laser beams and ion implantation appear more decisive. In the former case the solid surface is subjected to intense heating whose effects depend on the nature of the material as well as on the conditions of laser treatment.[13,14] In the latter case, the surface is subjected to mechanical damage, which can adequately simulate the formation of very small particles.[15]

In the specific case of RuO$_2$ electrodes, apart from γ-irradiation whose effects have not been conclusive to gain insight into the electrocatalytic properties,[14] preliminary experiments with laser and ion implantation, carried out long ago in this laboratory,[16] anticipated promising results that were not pursued further immediately. Since then, there were very few attempts with RuO$_2$. Actually laser was used as a source of heat to obtain the oxide from the precursor more quickly than with a standard procedure of thermal decomposition,[17] but never (to the best of our knowledge) to modify pre-formed RuO$_2$ electrodes.

In the case of ion implantation, there has been only one attempt thus far (to the best of our knowledge) to treat pre-formed RuO_2 electrodes.[18] The results reported cannot however be considered as conclusive for several reasons. More specifically: (i) Metallic ions were implanted with the possibility of creation not only of mechanical damages but also that implanted ions become active sites themselves; (ii) While an accurate physical analysis of the fate of implanted ions was carried out, the electrochemical analysis has been very qualitative without any mechanistic discussion, and any attempt at the separation of electronic effects from geometric effects.

In the above context, we have expanded our preliminary experiments[16] by treating RuO_2 layers on Ti, obtained by thermal decomposition, separately with a laser beam and ion implantation. With the aim to obtain surface defects only and to avoid implantation of foreign metal ions, RuO_2 was bombarded with krypton. Eventual modifications in electrochemical properties were investigated with standard techniques such as cyclic voltammetry and potentiostatic curves using O_2 evolution in acidic solution as a probe of surface electrocatalytic activity. Particular care has been placed in scrutinizing the possibility of separating electronic from geometric effects.

2. Experimental

RuO_2 layers were supported on Ti platelets of 5×5 mm size. The support was first etched in boiling oxalic acid for 1 h to dissolve any natural surface oxide.

2.1 *Electrodes*

RuO_2 thin layers were prepared by thermal decomposition of Ru nitrate at 400°C.[19] The precursor was dissolved in isopropanol and the solution spread over the support by brushing. The procedure introduced by Lodi *et al*[20] was adopted to obtain layers as smooth and compact as possible. After depositing a layer of solution onto the support, the solvent was evaporated at about 80°C in air and the electrode fired in a pre-heated oven for 10 min. Back from the oven and cooled down, the RuO_2 layer was gently scraped with filter paper to remove loose particles and cleaned up ultrasonically. The procedure was then repeated until an amount of about 1 mg cm^{-2} was attained.

The growth of the layer was checked by weighing. Fresh electrodes were characterized by cyclic voltammetry (see later on) before subjecting the specimens to the surface treatments.

Twelve samples were prepared and six of these were selected for further experiments. The choice was simply based on the closest similarity of physical and electrochemical features. Three electrodes were subjected to laser irradiation, two implantation, while the sixth sample was used as such to constitute a reference standard.

2.2 *Surface treatments*

Surface treatments were carried out in the National Laboratories of the National Institute of Nuclear Physics (INFN) at Legnaro (Padua, Italy). The energy of laser radiation was varied from 0·5 to 1·5, to $2·5 \text{ J cm}^{-2}$ for the three electrodes used. After the treatment the samples were used as such for voltammetric experiments.

Surface bombardment was operated with a beam of Krypton in a 200 KeV implantation apparatus. The dose of atom implantation was 10^{15} and 10^{16} cm^{-2}, respectively, for the two electrodes used. The samples were used as such after the treatment for voltammetric characterization.

2.3 *Solutions*

All electrochemical experiments were conducted in $0·5 \text{ mol dm}^{-3}$ H_2SO_4 aqueous solutions at $25 \pm 0·1°C$ in a water thermostat. Solutions were deareated by bubbling purified N_2 for not less than 30 min before experiments. The water used to prepare solutions was obtained from a Millipore-Milli Q distillation apparatus.

2.4 *Reference electrode*

Electrode potentials were measured and are reported with respect to a hydrogen electrode in the same solution (RHE).

2.5 *Electrochemical techniques*

2.5a *Instrumentation:* All electrochemical experiments were carried out using a Mod. 553 AMEL potentiostat/galvanostat equipped with a Mod. 667 AMEL electrometer for the measurement of elec-

trode potentials, and a Mod. 863 AMEL X-Y re-corder. The four-compartments electrochemical cell contained two Pt counterelectrodes separated from the central compartment of the working electrode by glass frits. The compartment of the reference electrode was connected to the surface of the working electrode via a Luggin capillary.

2.5b *Cyclic voltammetry:* The electrode potential was scanned between 0·4 and 1·4 V (RHE) at 20 mV s^{-1}. Voltammetric curves were recorded when stabilized (>5 cycles). Voltammetric charges were obtained by graphical integration of the voltammetric curves. The values reported later on are the mean of cathodic and anodic charges, as a rule closely balanced.

Voltammetric curves were recorded (a) for fresh samples, (b) for samples after surface treatments, (c) for samples after O$_2$ evolution polarization curves, and (d) for samples after determination of the reaction order with respect to H$^+$.

2.5c *Polarization curves:* Quasi-stationary potentiostatic curves were recorded between 1·30 and 1·60 V (RHE) by stepping the potential of 20 mV and reading the current after 2 min at each potential. At 1·60 V the direction of potential scan was reversed and experiments continued until the current became cathodic.

The reaction order with respect to H$^+$ for the anodic O$_2$ evolution was determined by recording polarization curves at different concentrations of H$_2$SO$_4$ (0·05, 0·1, 0·2, 0·3, 0·4, 0·5 mol dm^{-3}) at constant ionic strength by addition of Na$_2$SO$_4$. The order of reaction was derived from plots of log *j* (current density) at 1·46 V (RHE) vs pH. The value of potential was selected so as to lie on the linear section (Tafel region) of the polarization curves.

3   Results and discussion

3.1   *Voltammetric curves*

Figure 1 shows typical voltammetric curves of RuO$_2$ electrodes[4] before and after surface treatments. The most immediate observation is that both surface treatments enhance the current without changing the shape of the curves substantially. This suggests that the nature of surface redox transitions is not affected by the surface treatments. Nevertheless, in the case of atom implantation (curves b), the enhancement

observable at $E > 1·2$ V indicates higher electrocatalytic activity for anodic reactions. This is much less evident in the case of laser treatment (curves a).

3.2   *Voltammetric charge*

Integration of the curves in figure 1 gives the surface charge spent in redox transitions. For RuO$_2$ electrodes, the latter can be sketched as follows:[8]

$$RuO_x(OH)_y + \delta H^+ + \delta e \rightarrow RuO_{x-\delta}(OH)_{y+\delta}. \quad (1)$$
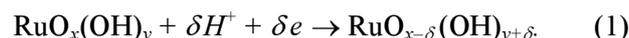
Equation (1) shows that the voltammetric charge (q^*) measures the amount of protons exchanged between the oxide surface and the aqueous solution. Thus, q^* is proportional to the surface concentration of active sites, i.e. to the actual active surface area.[5]

Since different fresh electrodes were used for different doses of surface treatments, the most convenient
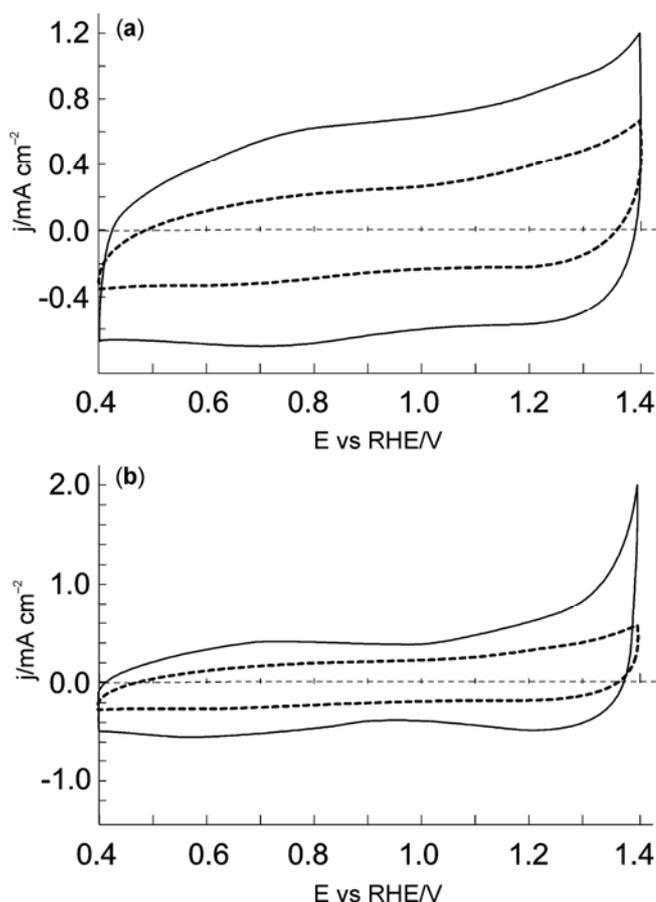

Figure 1.   Representative cyclic voltammetric curves of RuO$_2$ electrodes in 0·5 mol dm^{-3} H$_2$SO$_4$ aqueous solution. (**a**) Sample subjected to laser irradiation; (**b**) Sample subjected to Kr bombardment. (-----) Before surface treatment. (———) After surface treatment.

way to monitor the effect of treatments on surface charge is to compute the variation of $q*$ with respect to the fresh surface. Figure 2 shows the variation of $(\Delta q*/q_b*) \times 100$, where subscript 'b' stands for 'blank', as a function of laser treatment. The surface charge is seen to increase dramatically with the intensity of the treatment, levelling off at higher intensity. Quantitatively the surface charge increases by more than two times.

The surface charge is seen to increase also in the case of atom implantation. Quantitative data are not reported in a graph for two reasons: (i) The number of samples is small, and (ii) the increase is not monotonic, exhibiting a maximum for the lower dose. At any rate, the highest value of $\Delta q*$ is comparable for the two surface treatment procedures.

Increase in $q*$ can be regarded as increase in surface concentration of active sites. Nevertheless, laser treatment and atom implantation are not expected to produce similar physical and mechanical
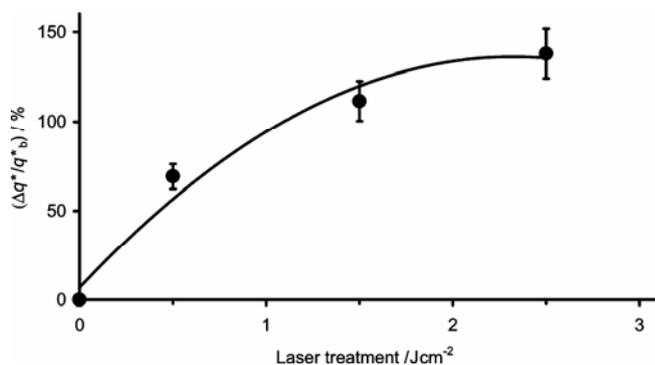

Figure 2. Increment of voltammetric charge relative to the pristine surface state as a consequence of laser irradiation.
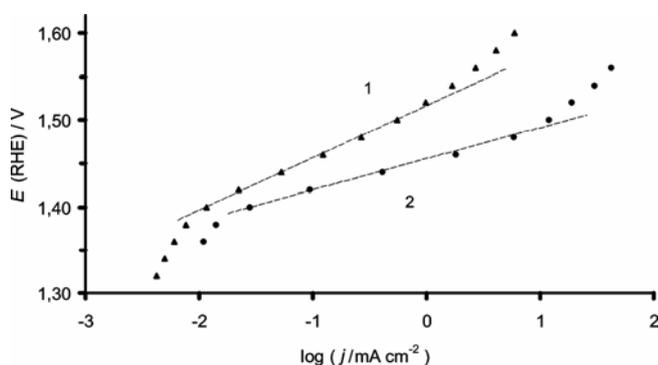

Figure 3. Current-potential potentiostatic curves for O_2 evolution on RuO_2 electrodes in 0·5 mol dm^{-3} H$_2$SO$_4$ aqueous solution. (1) Before surface treatment; (2) After Kr bombardment with a dose of 10^{16} cm^{-2}.

effects on an oxide surface. A laser beam produces a local intense heating whose first approximation effect on a crystalline solid should be amorphization. The latter however should result in decrease of surface charge as in the case of melting of a rough solid surface. It is equally possible to look at laser effects in the other way round. Oxides produced by thermal decomposition are poorly crystalline and a heating pulse could induce crystallization. The high intensity of the beam much probably causes a violent thermal shock with formation of surface microcracks.[14] As a consequence, the number of surface sites accessible to the solution increases.

The interpretation of the data obtained with atom implantation is more straightforward. The surface bombardment has a strong mechanical effect with breakage of microcrystallites and formation of nanosized surface defects.[18] Macroscopically the final effect is the same as for laser treatment with a sizeable increase in surface charge. But the nature of the surface sites created by the two surface treatments turns out to be different, as shown in the next paragraphs.

3.3 Tafel lines

Figure 3 shows typical quasi-stationary current-potential curves for O_2 evolution on fresh vs atomimplanted electrodes. The experimental data have not been corrected for ohmic drop effects. Nevertheless, a linear portion of the curves (Tafel region) can easily be identified. There is no doubt that atom implantation enhances the current at constant potential. It is also evident that the activity enhancement is not attributable to surface area effects (geometric factors) only, in that the slope of the linear section (Tafel slope) changes with surface treatment. Since the Tafel slope is an intensive quantity, it depends on the reaction mechanism only and not on geometric factors.

3.4 Tafel slope

Figure 4 illustrates the effect of laser irradiation on the Tafel slope for O_2 evolution. For the fresh electrode the Tafel slope is around 60 mV, decreasing with laser treatment. It is intriguing that the decrease of the Tafel slope (b) levels off at higher laser intensity, clearly showing parallelism with the behaviour of the surface charge in figure 2. This suggests that the origin of the variation of $q*$ is the same as for

the change in b, although geometric factors are involved in the former case, and electronic factors in the latter.

Figure 5 shows that a quite similar picture of b vs surface treatment is observed with atom bombardment. There are however two notable differences: (i) The decrease in b is monotonic, differently from q^*, and (ii) the Tafel slope decreases more appreciably than in the case of laser treatment. This indicates that for atom implantation electronic effects prevail over geometric effects.

3.5 *Reaction order*

Figure 6 shows a typical plot of $\log j$ vs pH to obtain the reaction order with respect to H^+ (β_{H^+}). The experimental points are well-aligned with correlation coefficients around 0·99. This indicates that eventual variations of reaction order by more than 0·1 are
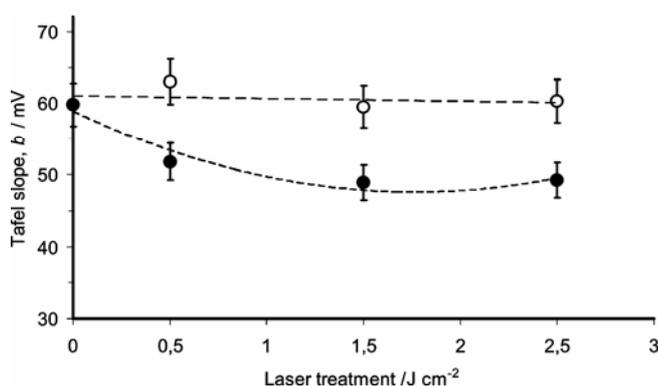

Figure 4. Tafel slope for O_2 evolution on RuO_2 electrodes as a function of laser irradiation. (O) Before treatment; (●) After treatment.
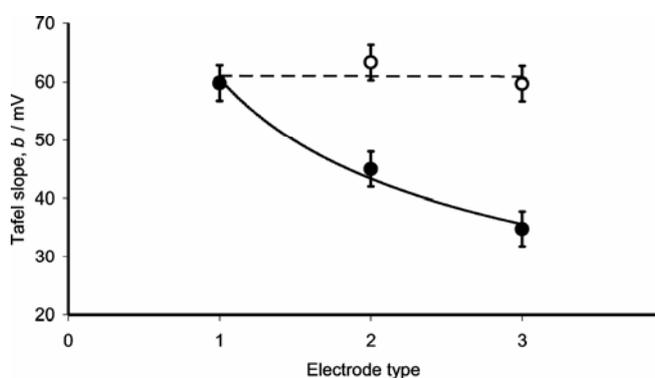

Figure 5. Tafel slope for O_2 evolution on RuO_2 electrodes as a function of Kr bombardment. (1) Untreated (blank) sample. Kr dose: (2) 10^{15} cm^{-2}; (3) 10^{16} cm^{-2}. (O) Before treatment; (●) After treatment.

real. Since both Tafel slope and reaction order depend on the reaction mechanism, a correlation is expected between the two quantities. This is confirmed by the plot in figure 7 showing b vs β_{H^+}. While b varies from 60 mV to <40 mV, the reaction order changes from ca 1 to ca 1·7.

Fractional reaction orders are not chemically significant since they include double layer effects.[21] In the case of oxide electrodes, as pH is changed to determine the reaction rate as a function of pH, the surface charge is modified because of the specific mechanism of surface charging. The latter is the origin of double layer effects. These aspects have been exhaustively discussed by one of us in previous papers.[22,23] Therefore, the picture in figure 7 is in line with the known behaviour of oxide surfaces and the plot possesses full significance.

3.6 *Reaction mechanism*

The Tafel slope for blank RuO_2 (ca 60 mV) is in agreement with previous work.[24] The Tafel slope for
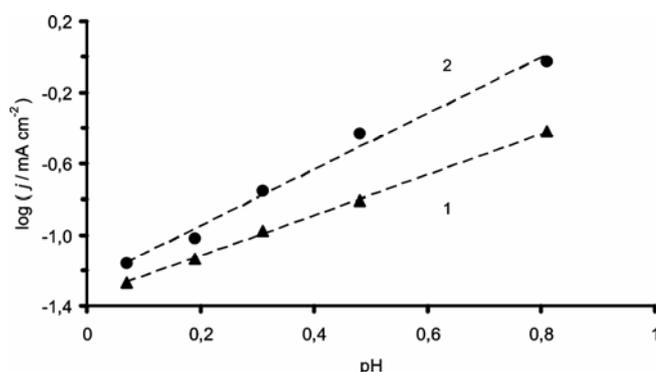

Figure 6. Typical plots of $\log j$ (at 1·46 V) vs pH for the determination of the reaction order of O_2 evolution. Surface treatment: (1) laser irradiation, 0·5 J cm^{-2}; (2) Kr bombardment, 10^{16} cm^{-2}.
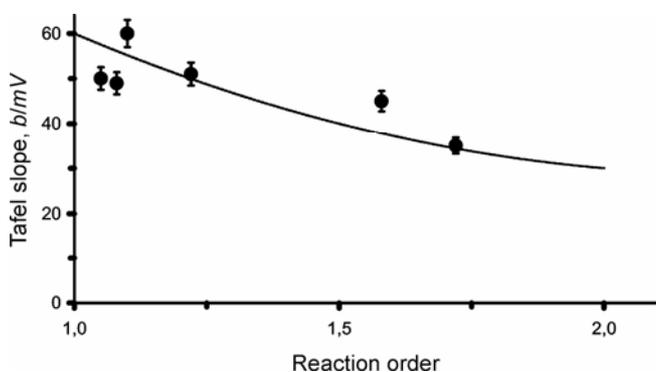

Figure 7. Graphical correlation between Tafel slope and reaction order for O_2 evolution.

O_2 evolution has been found to vary from 30 mV for nanocrystalline surfaces up to 60 mV for the (110) face of single crystals.[5,9] The 60 mV of this work indicates that blank fresh electrodes possess rather smooth surfaces with a small number of surface defects. Surface treatments increase the number of surface defects that offer more active surface sites. As a consequence the Tafel slope decreases and the apparent current density increases.

For O_2 evolution on oxide electrodes a generalized mechanism has been previously proposed by one of us:[25]

$$-S\text{-}OH + H_2O \rightarrow -S\text{-}OH(OH)^* + H^+ + e, \qquad (2)$$

where $-S\text{-}OH$ is a surface active site, and OH^* is an unstable intermediate readily converted into a more suitable species (spillover):

$$-S\text{-}OH(OH)^* \rightarrow -S\text{-}OH(OH). \qquad (3)$$

The surface complex is then further oxidized:

$$-S\text{-}OH(OH) \rightarrow -S\text{-}OH(O) + H^+ + e, \qquad (4a)$$
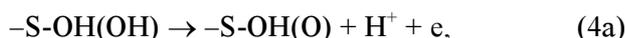
or, alternatively, two adjacent surface complexes recombine:

$$-S\text{-}OH(OH) + -S\text{-}OH(OH) \rightarrow 2-S\text{-}OH(O) + H_2O. \qquad (4b)$$
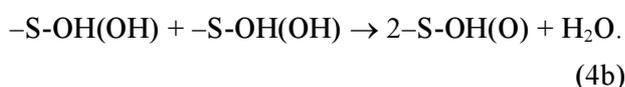
Finally, the surface species formed in steps (4) decomposes releasing gaseous O_2:

$$-S\text{-}OH(O) + -S\text{-}OH(O) \rightarrow 2-S\text{-}OH + O_2. \qquad (5)$$
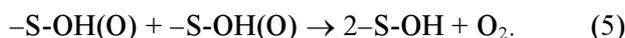
According to the data in figure 7, step (3) prevails as a rate determining step on blank RuO_2, step (4a) on laser treated RuO_2, and step (4b) on atom implanted RuO_2. The variable that changes with surface treatments is in the end the heat of adsorption of oxygenated intermediates on the electrode surface.[26] The heat of adsorption depends in turn on the nature of the surface active site. The experimental picture points to an increment of the electrode-intermediate bond strength as surface defects change from the blank electrode to laser and finally to implantation treatment. In other words, surface treatments promote real electrocatalytic effects, and atom implantation is more effective than laser irradiation.

3.7 *Electrocatalysis*

Unquestionable evidence of real electrocatalysis (electronic effects) can be obtained by eliminating geometric effects related to variations in surface area. This can be achieved either (i) by resorting to intensive quantities or (ii) by allowing for surface area effects in extensive quantities.

Scrutiny of experimental data based on approach (i) above has been performed in the previous sections. In this section, analysis will be made of the apparent current density (the apparent reaction rate) that by its nature is an extensive quantity, i.e. it depends straightforwardly on the extension of the surface area.

Figure 8 shows a plot of the apparent reaction rate (at 1·46 V) as a function of the nature of the electrode, a non-quantitative variable. It is evident that the reaction rate increases with laser irradiation and more with atom implantation. However, the increment does not vary appreciably with laser treatment, whereas rises sharply with implantation.

The data in figure 8 encompass both electronic and geometric effects and cannot be used to conclude about electrocatalytic effects. Nevertheless, the activity of electrocatalysts is mostly discussed in the literature on the very basis of raw reaction rate data.

Oxide electrodes offer the possibility of allowing for surface area effects on the basis of the voltammetric charge, q^*.[27] Figure 9 shows a plot of the relative increment in reaction rate at 1·46 V against the relative increment in surface charge. If only surface area effects were operating, doubling of q^*
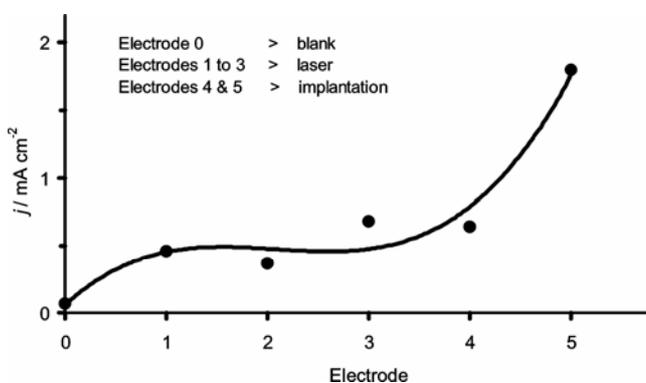

Figure 8. Current density for O_2 evolution vs. the kind of surface treatment. (O) Blank; (1, 2, 3) laser irradiation, increasing dose; (4, 5) Kr bombardment, increasing dose.
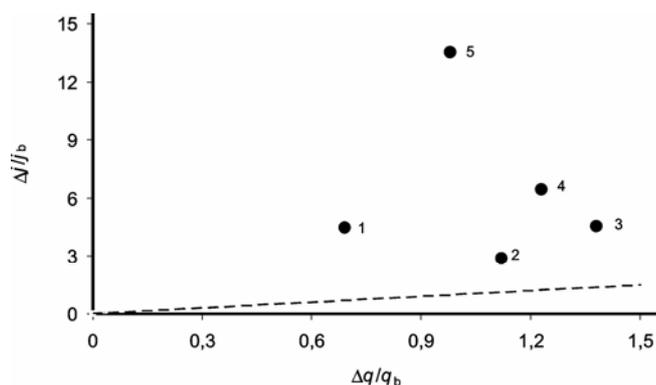
Figure 9. Relative increment of current density for O_2 evolution at 1·46 V vs the relative increment of voltammetric charge. Subscript 'b' stands for 'blank'. (1) Blank electrode; (1, 2, 3) Laser irradiation, increasing dose; (4, 5) Kr bombardment, increasing dose.

would result in doubling of j. Therefore, pure surface area effects would produce experimental points lying on a straight line (of unit slope in case relative increments are plotted – the dashed line in figure 9). On the contrary, all electrodes after surface treatments give points lying away from the straight line, more specifically above, i.e. the reaction rate increases more than expected on the basis of geometric effects only.

The data in figure 9 points to true electrocatalytic effects for all electrodes, but while these are moderate and substantially constant for laser irradiation, they are stronger and dependent on the dose of implanted species for atom implantation. This confirms once more that atom implantation gives rise to more active surface sites than laser irradiation.

4. Conclusions

(i) Both laser irradiation and atom bombardment enhance the apparent electrochemical activity of RuO_2 electrodes. (ii) Geometric effects can be assessed on the basis of the voltammetric charge, assumed to be proportional to the surface concentration of active sites. Electronic effects can be assessed on the basis of the Tafel slope for O_2 evolution (an intensive quantity), as well as of correlations between current density and voltammetric charge. The latter depends only on geometric factors, the former on both geometric and electronic factors. (iii) Scrutiny of the experimental data reveals that most of the apparent activity enhancement is related to electronic factors.

Geometric factors lead to double the activity at most. (iv) Both surface treatments enhance the true electrocatalytic activity, but the enhancement is definitely higher for atom bombardment. (v) Atom bombardment is presumed to stimulate the exposition of particularly active sites as a consequence of the fracture of RuO_2 crystallites. (vi) Laser irradiation is thought to cause rapid crystallization leading to some disorder in the crystallites accompanied by cracking due to violent heating.

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