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Current efficiency losses in indirect electrochemical processing

A. T. KUHN

Eastman Dental Hospital, 256 Gray's Inn Road, London WC1, UK

M. BIRKETT

L. B. Holliday Ltd., Leeds Road, Huddersfield, Yorks, UK

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The various reasons for current efficiency losses in indirect electrochemical processing are considered. Using the Cr(VI) oxidation of *o*-toluene sulphonamide as a model, it is shown that accretion of organic residues is an important factor contributing to current efficiency losses. Other evidence is provided to suggest that film formation on the electrode surface acts selectively to promote oxygen evolution rather than Cr(III) re-oxidation.

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1. Introduction

A number of publications devoted to indirect electrochemical processing have appeared [1–7] and consider various aspects of the idea in which a 'carrier' is electrochemically oxidized or reduced and then allowed to react chemically with the substrate to form the required product. A re-appraisal of these publications suggests that too much emphasis is laid on the advantages of the idea, and too little, indeed nothing at all, has been said regarding the drawbacks of the method. One of the greatest practical drawbacks is the frequently unexpected loss in current efficiency observed in working processes. To redress the balance in the literature, we wish to report on some practical observations regarding this phenomenon.

In a divided electrochemical cell, one is entitled to expect that the inorganic carrier ion will be oxidized at the anode with an efficiency limited only by considerations of mass-transport. In practice, it is found that current efficiencies are far lower. As we shall see, the efficiencies obtained for oxidation of un-contaminated Cr^{3+} solutions as cited in [18] can be very difficult to obtain in practical installations, and such factors can lead to major revision of cost and viability estimates.

Analysis of the causes of loss in current efficiency leads to two main types of inefficiency, namely electrode poisoning and carry-over of organic material.

2. Electrode poisoning

A selective increase in overpotential for the carrier oxidation process is observed without a commensurate increase in oxygen evolution overpotential.

3. Carry-over of organic matter

It is found that appreciable concentrations of organic matter can be detected in the anode compartment of a cell ostensibly oxidizing metal ions to their higher valence state and thus detracting from the efficiency of this process by affording a competitive reaction. Most industrial indirect processes are based on the 'ex-cell' process, i.e. the oxidized carrier reacts with the feedstock in a separate vessel and when reaction is complete, a separation of product and spent liquor takes place. It is notable that all known full-scale indirect processes are based on solid reactants and products and filtration is thus the ideal method for separation of the two phases at the end of the reaction. However organic, oxidizable, material can still be carried-over with the spent liquor back to the electrochemical cell. Such material can arise because of soluble impurities in the feedstock, or

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the presence in the aqueous medium of unreacted feedstock, product, partial oxidation products, or a metal-organic complex.

Whatever the species carried-over, the probability is that it will be totally oxidized to CO_2 in the electrochemical cell as a result of prolonged and efficient contacting with the PbO_2 anodes which are at present universally used in these cells. In contrast to the three-electron oxidation (Cr^{3+}) or one electron (Ce^{3+}) oxidation of the carrier species, the total oxidation of carried-over organics can involve 20 or 30 electrons. Thus small amounts of organic will absorb inordinately large amounts of coulombic charge. Returning to the five classes listed above, the following comments can be made.

3.1. *Soluble impurities in the feedstock*

Chromic acid is industrially used to oxidize various polynuclear hydrocarbons. Pyrene of widely varying purity is available from a range of sources. Pyrene of guaranteed 90% purity results in Cr^{3+} re-oxidation efficiencies of only 50%, whereas the use of 95%+ grade gives better than 80% current efficiency in subsequent chromium (III) re-oxidation.

3.2. *Unreacted feedstock*

In most indirect processes, care is taken that excess oxidant is added to the feedstock. The likelihood of unreacted feedstock passing back through the filtration system to the electrochemical cell is thus extremely small. Moreover, the solubility of polynuclear aromatic hydrocarbons in aqueous media is so slight that this effect can be neglected for this type of system.

3.3. *Product carry-over*

The quinonoid products formed by oxidation of the hydrocarbons, are considerably more soluble than their precursors, and carry-over of such species must therefore be expected.

3.4. *Partial oxidation products*

Unpublished work [19] on the oxidation of naphthalene by Cr(VI) indicated that naphthaquinone was formed but only in some 50% yield. The balance was a highly soluble keto-acid which would all have been returned to the cell. Based on the foregoing, it will be appreciated that such a situation would lead to current efficiencies of 5–10% since total oxidative destruction of the keto-acid would be predicted.

3.5. *Metal-organic complex formation*

The possibility of (soluble) metal-organic complexes being formed, with obvious consequences, must be considered. Chromium, the most widely used carrier, is equally well known for its ability to form complexes, notably with aromatic carbonyl compounds [8, 9] but these are Cr(0) or Cr(I) valence species and so unlikely to occur in oxidative systems.

4. Practical examples of current-efficiency losses

The only published example of loss of current efficiency in indirect processing of which we are aware is found in publications of Mizuguchi [10–13] which have been translated for us from the Japanese. It was shown that when *o*-toluene sulphonamide was oxidized by chromic acid to saccharin, there was a decrease in the current efficiency determined in the second and subsequent Cr^{3+} re-oxidations as compared with the initial oxidation. Furthermore a yellow deposit and damage to the electrode surfaces was reported. Mizuguchi also found a white precipitate on completion of electrolysis but the latter was not a decomposition product of saccharin which proved to be stable to further oxidation by Cr(VI). The cause of the reduction in current efficiency was not further investigated by these authors, who contented themselves with finding a partial solution to the problem. This lay in increasing the sulphuric acid concentration and using an excess of Cr(III). Nevertheless, current efficiencies for the re-oxidation of chromium were still lower (60–70%) than those found in the initial oxidation (95% or more).

Trivalent manganese salts have been used as indirect oxidants for benzaldehyde production from toluene, and here too, purification has been found necessary [14] to achieve high current efficiencies in re-oxidation but the cause of the effect has not been studied.

In the present work, we have extended the work of Mizuguchi, which was essentially qualitative, to investigate the relative importance of the various effects listed above, on loss of current efficiency. The chromium (III)–*o*-toluene sulphonamide system was therefore chosen as a model for this purpose.

5. Experimental

o-toluene sulphonamide was prepared by the chlor-sulphonation of toluene at – 5 to 0° C. The ortho- and para-substituted species were separated by freezing, the ortho product was then aminated and recrystallized from methanol.

A stock solution of Cr(VI) was prepared, consisting of 1 M CrO_3 in 6 M H_2SO_4 (all GP Grade). A portion of this solution was used to oxidize *o*-toluene sulphonamide at 55° C after which it was filtered. The organic was present in excess. The resulting Cr^{3+} solution was used in the re-oxidation experiments.

A second portion of the stock solution was electrochemically reduced to Cr^{3+} in a divided cell fitted with Pb electrodes, and this solution, which had at no time been exposed to organic species, formed the control experiment.

The two solutions were then oxidized in a parallel plate cell of 200 cm^2 electrode area. Anolyte and catholyte were separated by an ion exchange membrane (Nafion 427, cationic) and a lead cathode and preformed PbO_2 on Pb anode were used. Solutions were circulated through the anode compartment with an Iwaki MD 15 centrifugal pump at a rate of 8 l min^{-1}.

The solutions were maintained at 30° C and a current density of 15 A dm^{-2} was used. After completion of each electrolysis, the cell was filled with dilute sulphuric acid and a low current was imposed across the terminals to prevent reduction of the PbO_2 at the anode. During electrolyses, samples were withdrawn from the 2 l reservoir and the Cr(VI) content was analytically determined by reaction with excess Fe^{2+} and back-titration with $KMnO_4$.

6. Results

Fig. 1 shows the progress of the anodic re-oxidation of the Cr^{3+} from the uncontaminated and contaminated solutions. In order to eliminate any effects due to possible degradation of the electrode, or formation of permanently blocking species upon it, the control solution was re-oxidized first, then the organic-contaminated solution, and finally a further sample of the control solution. Apart from slight differences due to the instability of fully-formed PbO_2 surfaces, it is seen that the first and last runs are virtually coincident, thus providing clear evidence that the much lower current efficiencies observed during the oxidation of the organic-contaminated solution, arise from electrode reactions of species in solution and are not caused by changes on the anode surface.

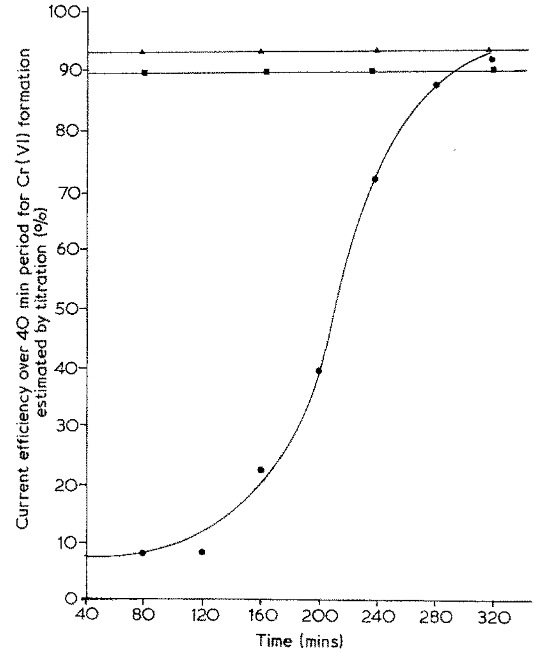


Fig. 1. Current efficiencies in the regeneration of Cr(III) solution. ▲■ control solutions; ● solution contaminated with organic. [Note that the solution was approximately 50% depleted in Cr(III) at the end of the experiment.] Total current was 30 A, 30° C, current density 15 A dm^{-2}.

6.1. *Scanning electron microscopy and EDAX measurements*

A series of experiments was conducted in which a run was carried out and the electrodes were withdrawn after 12, 120 and 360 min. Two series of experiments were carried out, the first with uncontaminated chromium solutions, the second using the contaminated solutions. Six separate

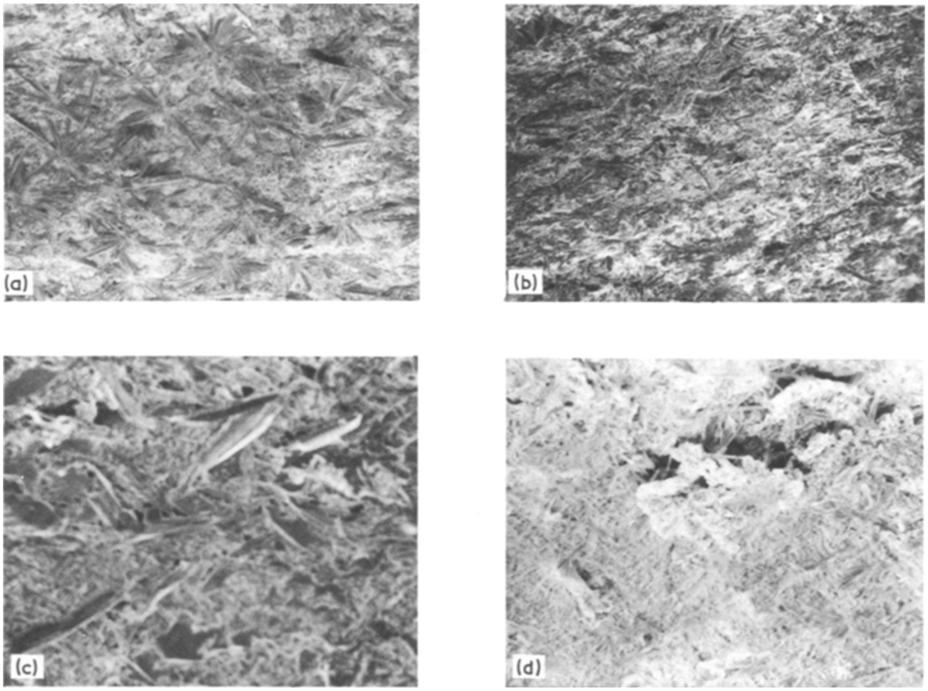


Fig. 2. SEM photographs of electrodes withdrawn from solution after electrolysis (× 320). A, 120 mins electrolysis, uncontaminated solution; B, 120 mins electrolysis, organic contaminated solution; C, 360 mins electrolysis, uncontaminated solution; D, 360 mins electrolysis, organic contaminated solution.

electrodes were therefore used. The scanning electron micrographs (see Fig. 2) show clearly that the surface texture is different in the two cases, and that the difference is most acute at the longest times. EDAX showed that Pb was present in all cases, but significant amounts of Cr were detected only in the case of both samples at 360 min.

6.2. *Gas evolution experiments*

The volume of gas evolved during a run was measured and a partial analysis for CO_2 was made, it being assumed that the remainder was oxygen. One litre samples of gas were drawn off at intervals. In the case of the uncontaminated solutions, only oxygen was found (Fig. 1). In the case of contaminated solutions, a typical analysis is shown in Table 1.

Table 1

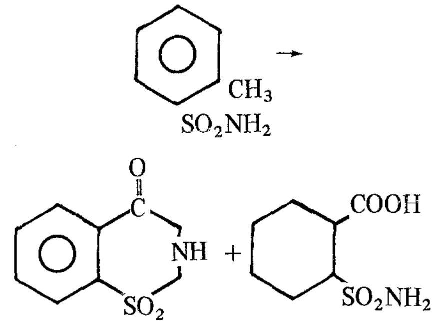
Time (min)	*Rate of total gas evolution* (cm^3 min^{-1})	*Rate of CO_2 evolution* (cm^3 min^{-1})
12	67	12
60	65	6
120	45	3
300	6	–

6.3. *Analysis of contaminated solutions*

A rudimentary analysis of the contaminated solutions was made by solvent extraction (three 100 ml chloroform extractions) of the solution and weighing the residue. On the basis that the molecular weight of the residue is 200, the concentration of organic species in the contaminated solutions was found to be 2×10^{-3} mole l^{-1}.

7. Discussion

Analysis of the data shows that both of the mechanisms mentioned in Section 1 are of possible importance, and play a significant role in this case. ‘Carry-over’ of organic material takes place, and the presence of this has been detected not only by solvent extraction, but also from the CO_2 evolved during the regeneration of the Cr(III). However, selective poisoning is also seen to be taking place; not only CO_2 but also far greater quantities of oxygen are evolved than at comparable stages in the process using uncontaminated solutions. Finally, the SEM and EDAX records show that differences in electrode surface texture and composition are observable in the two cases. The 'carry-over' process can be treated by normal equations for diffusion-controlled processes. If it is assumed that the products of *o*-toluene sulphonamide oxidation are mainly saccharin with traces of *o*-sulphonamide benzoic acid



MW = 183 I

MW = 220 II

we may take 200 as being the molecular weight of the organic species in solution, and this approximation is further aided by the fact that if the estimate is in error either on the high or low side, the number of electrons involved in the oxidation will broadly change in the same direction. The oxidation of either of these compounds to CO_2 proceeds as follows:

$$\mathrm{I} + 15\,H_2O \rightarrow 7CO_2 + (NH_4)_2SO_4 + 26\,H^+ + 26e$$

$$\mathrm{II} + 15\,H_2O \rightarrow 7CO_2 + (NH_4)_2SO_4 + 24\,H^+ + 24e$$

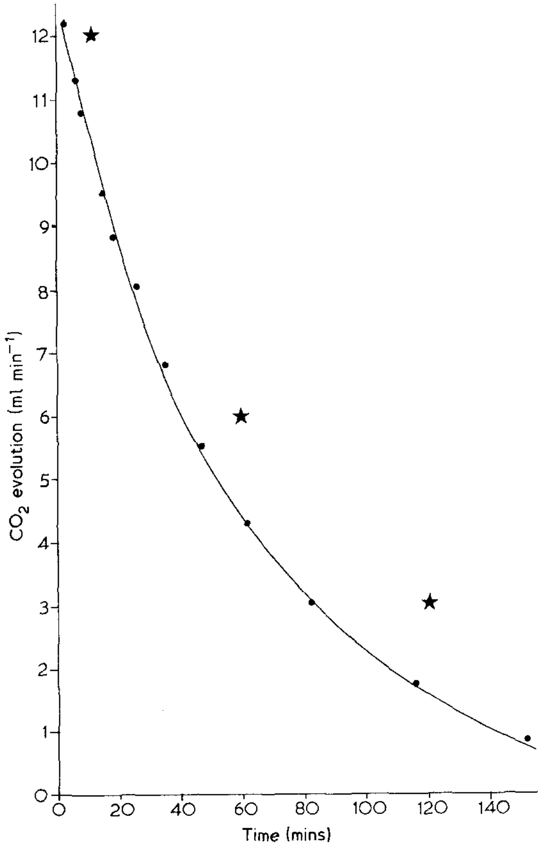


Fig. 3. Predicted (●) (Equation 1) and measured (★) rates of CO_2 evolution. Conditions as in Fig. 1 using solution contaminated with organic.

from which it can be seen that 25 Faradays per mole is a reasonable assumption. Using the equations [15]:

$$\log i_{t=t} = \log i_{t=0} - \frac{0{\cdot}434DAt}{V} \qquad (1)$$

where

$$i_{t=t} = \frac{nFDC_t}{\delta} \text{ and } i_{t=0} = \frac{nFDC_0}{\delta}$$

the value for δ was obtained from [17] and with the value C_0 determined by solvent extraction, values of C_t the concentration of organic species as a function of time could be obtained. Hence one may estimate the partial current due to organic oxidation, i_t, and the rate of CO_2 gas evolution. Fig. 3 shows this calculation plotted out with the experimental points superimposed. Agreement is seen to be very satisfying. The assumption that the oxidation is total (to CO_2) has been questioned, and it is true that PbO_2 anodes are used in electro-organic oxidations where, for example, benzene is oxidized to benzoquinone. However there is evidence that [20] as the current density is increased to a limiting value, the total oxidation process predominates. The selective poisoning process, though clearly enough seen from the data in Table 1, is less amenable to quantitative treatment. Inspection of the SEM photographs clearly reveals the very different structure of the surface deposit when organic compounds are present. But whether this is a finer form of PbO_2 or chromate, or whether a thin covering of organic is present, it is not possible to judge. The samples appeared to the eye to have a brownish-yellow 'dusty' appearance which we assume was chromate. It is possible that organic layers, if formed, would be removed in the high vacuum of the SEM.

In conclusion, we have attempted to point out that unexpected current efficiency losses can take place in indirect electro-organic processing. We have discussed the various ways in which such losses can occur. Taking the indirect oxidation of *o*-toluene sulphonamide to saccharin as an example, we have shown that several distinct processes are at work. One question remains open. While one can conceptually distinguish between 'carry-over' of organics and 'selective' electrode poisoning, it might still be argued that there is a relationship between the two in that the surface film which is responsible for the selective action must be formed from the organic species in solution. Once this has been substantially removed by anodic oxidation, there is evidence from the table that the organic layer is itself destroyed by oxidation in that after 300 min, the selective action appears to have virtually ceased, with Cr(III) being oxidized in preference to water, as is the case in the pure solutions.

The implications of our work for proposed novel electro-organic indirect syntheses are clear. The solubility of the organic reactant in the carrier electrolyte must be determined and efforts must be made to keep its concentration at the lowest possible level.

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