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Coelectrodeposition of aluminium and cadmium from aqueous sulphate solutions

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Coelectrodeposition of aluminium and cadmium from aqueous solutions is shown to be possible under very restricted conditions. The deposits are in a divided form and contain up to 40% aluminium. Lower cadmium ion concentration in the solutions leads to a higher proportion of aluminium in the deposit and there is an optimum concentration for the sulphuric acid in solution. Faradaic yields for metal electrodeposition are, however, low and hydrogen evolution is the predominant reaction.

1. Introduction

Light metals such as magnesium and aluminium have long been considered for use as negative electrodes in electrochemical energy conversion devices. The theoretical capacity is very high and much work has been devoted to the study of the mechanism and feasability of primary batteries using these metals as electrodes. Aluminium has been investigated particularly for inclusion in metal-air power sources.

However, aluminium was not considered for secondary batteries in aqueous solutions since no practical technique for the electrodeposition of the metal in such solutions was available, only a German patent [1] from 1969 has claimed that a secondary aluminium electrode can be obtained in sulphate solutions but it gave few details.

We have now investigated further the possibility of the electrodeposition of aluminium from aqueous sulphate solutions.

2. Experimental procedure

For convenience a solution with a single anion present was chosen: sulphate ion. Several sulphate salts were dissolved in high concentration sulphuric acid solutions, the density of which, d, measured at 25° C in g cm^{-3}, has been used for the determination of the acid concentration. Although its solubility is very low, saturated solutions of aluminium sulphate were used as the electrolyte. Other metal sulphates: cadmium and magnesium, were used as additives in our experiments.

All the experiments were made at room temperature in an argon or nitrogen atmosphere containing no more than 10 ppm of oxygen. The electrode was made of pure aluminium sheet with impurity level less than 10 ppm and, before each experiment the aluminium surface was cleaned in hydrochloric acid, rinse with conductivity water, then treated in the electrochemical cell itself by a potentiostatic pulse sequence or by cathodic polarization at − 2.0 V versus SCE. This treatment proved to be necessary in order to obtain reproducible results and is assumed to have removed the oxide film from the electrode surface. The electrodeposition experiments were carried out under constant current conditions, with an apparent current density averaging 1.5 mA cm^{-2}.

The experiments were directed towards obtaining systems which could be used as secondary battery electrode, and no structural study of the deposits has been made.

The composition of the deposits obtained has been determined qualitatively by UV emission spectroscopy and quantitatively by complexometric and polarographic techniques. UV spectroscopy shows the presence of aluminium in the deposits but gives no precise quantitative information; the amount of aluminium in the deposit was determined by complexometric analysis whenever the amount of deposit allowed. When the latter was too small, UV spectroscopy having

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shown that the only metals present in the deposits were aluminium and cadmium, their concentrations were determined by polarography of cadmium which was the most abundant of the two metals. There is some *a priori* uncertainty about the results obtained by this difference technique for the amount of aluminium deposited at the electrode. But when possible, the comparison with the results obtained by direct complexometric determination of aluminium, shows a very good agreement. This agreement proves that aluminium is not present as an oxide or an hydroxide and that it can be assumed to be in the metallic form.

These determinations lead to the calculation of the aluminium proportion in the deposit, p, and of the Faradaic yields of the electrodeposition experiments, Y_{Al}, for the electrodeposition of aluminium and, Y_M, for all metal electrodeposition.

The uncertainty in the percentage of aluminium in the deposit, Δp, has been calculated to be approximately ± 0.5%.

3. Results

All the deposits were obtained in a divided form, a texture which is very suitable for a secondary battery electrode. It allows easy removal from the surface of the electrode for analysis, but hydrogen evolving during the experiment may lead to the loss of part of the deposit through mechanical rupture, and to a low value for the Faradaic yield. Thus, in Table 1, only the highest value obtained from each set of parameters are reported.

The experiments show that aluminium electrodeposition is not possible from saturated solutions of aluminium sulphate in sulphuric acid, only hydrogen evolution occurs. In order to achieve deposition of aluminium, two additivies, magnesium and cadmium sulphate, were investigated and the influence of acid and additive concentrations in the electrolyte were then studied.

3.1. *Influence of magnesium concentration*

The German patent [1] indicated that the proposed electrolyte contained magnesium sulphate. In the various conditions tested and whatever the concentrations of the other compounds were, however, the magnesium ion concentration had no influence on the results. Certainly, no magnesium was found in any deposits. In the subsequent experiments electrolytes containing only cadmium and aluminium sulphates were used.

Table 1. Proportion of aluminium in deposit (wt.%), p, and Faradaic yield for aluminium electrodeposition, Y_{Al}, from aqueous sulphate solutions saturated with $Al_2(SO_4)_3$, as a function of acid and cadmium sulphate concentration; I = *1.5 mA cm*$^{-2}$

$d_{H_2SO_4}$ (g cm^{-3})	C_{CdSO_4} (g dm^{-3})	p (%)	Y_{Al} (%)	ΔY_{Al} (± %)
1.35	2	13	7.58	0.29
1.35	4	0.4	1.24	1.30
1.35	8	0.6	1.64	1.30
1.40	2.3	38	35.2	0.5
1.40	3.3	21.4	–	–
1.40	4	12	17.0	0.7
1.40	8	0	0	–
1.45	0.8	11.7	5.51	0.25
1.45	2	4.3	4.58	0.55
1.45	4	2	4.0	1.0
1.45	8	0.75	4.5	3.0

3.2. *Influence of cadmium concentration*

The presence of cadmium ions in solution leads to aluminium electrodeposition simultaneously with the expected cadmium deposition on the negative electrode. The experiments were directed towards the study of the relation between cadmium concentration and aluminium deposition, with the intention of obtaining the lowest proportion of cadmium in the deposit, as well as the highest Faradaic yield for aluminium electrodeposition.

For high cadmium concentrations in solution, the proportion of cadmium in the deposit and Faradaic yield for metal deposition Y_M increased, while Y_{Al} is low. For lower concentrations, down to 1 g dm^{-3} $CdSO_4$, a higher proportion of aluminium was found in the deposit; it can reach 40% and Y_{Al} appears to be higher as the aluminium proportion in the deposit increases. However, the Faradaic yield Y_M decreases and hydrogen evolution becomes predominant. Both Y_M and Y_{Al} go to zero without cadmium in the solution, and it is likely that a maximum, both for p and Y_{Al}, might be observed at very low concentration of cadmium ion, below 1 g dm^{-3} $CdSO_4$.

However, it was not possible to measure the value of p for these cadmium ion concentrations, since the amount of the deposit was too small for analysis. Thus, the maximum inferred from the experimental results might be only an artefact. p may increase to zero cadmium concentration, the minimal deposition observed for this value masking the formation of a very thin, possibly monoatomic pure aluminium layer which cannot be detected by our investigation techniques. Formation of hydride at the aluminium surface may account for stopping this reaction. In contrast the maximum of Y_{Al} must be real corresponding to an optimum value of $C_{Cd^{+2}}$.

The rôle of cadmium in the electrodeposition of aluminium is unclear but several possibilities can be considered.

Firstly, the deposition of cadmium will modify the hydrogen overvoltage of the electrode. Indeed, the hydrogen overvoltage is shifted from − 0.25 V versus SCE on platinum to about − 0.71 V versus SCE as soon as an electrodeposited layer of cadmium is present on a Pt electrode. With the aluminium electrode in contact with a sulphuric acid solution, however, the hydrogen overvoltage was already about − 0.74 V versus SCE (Fig. 1). Addition of cadmium sulphate to the solution does not modify this value and the influence of the cadmium ions cannot therefore be interpreted in this way.

Secondly, because of the lack of aluminium electrodeposition on an aluminium electrode in the absence of cadmium ions, it may be assumed that the deposition of aluminium occurs on the electrodeposited cadmium, and that the process goes on as long as cadmium ions are present in the solution. When the concentration of cadmium ions increases, its deposition current increases accordingly and the proportion of aluminium in the deposit will decrease. It can be seen in Table 1 that Y_{Al} is low in this case but its values cannot be determined accurately when p is lower than 4% and no definitive conclusions can be drawn from these results.

3.3. *Influence of acid concentration*

The greatest variations observed are related to changes of the acid concentration. The experiments were made using sulphuric acid solutions with concentrations between 4 and 12 mol dm^{-3} although aluminium deposition could be achieved only for concentrations around 7 mol dm^{-3} which correspond to densities varying roughly from 1.30 to 1.50; the final study was restricted to solutions whose density was 1.35, 1.40 and 1.45 g cm^{-3}. Results show that the percentage of aluminium in the deposit exhibits a maximum for $d = 1.40$ g cm^{-3}, and decreases either side of this value.

These results can be compared with corrosion of pure aluminium sheet in sulphuric acid solutions, in the absence of oxygen, dissolution of the metal was slowest for the 7 mol dm^{-3} solution, and it can be assumed that the maximum in the percentage of aluminium in the deposit is related to variations of the sulphuric acid solution characteristics.

Indeed, study of the variations of the electrical conductivity of the solution [2] shows a maximum of conductivity, which can be related to a maximum in H$^+$ ion activity and a maximum in the acid properties, for about 3.5 mol dm^{-3} solutions, and that increasing the concentration to around 7 mol dm^{-3} leads to a decrease of the electrolytic conductivity, which must be correlated with decreasing acid properties. On the other hand, the oxidising properties increase with concentration and the optimum value for the aluminium

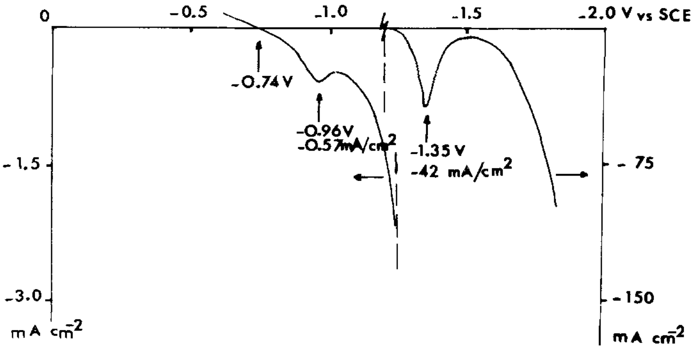

Fig. 1. *I–E* curve on Al electrode in H_2SO_4, $d = 1.41$, $Al_2(SO_4)_3$ saturated.

deposition could possibly correspond to the acid concentration for which the cumulative effects for these two properties are at their lowest value, thus lessening the corrosion reactions of aluminium.

This optimum value could also be related to competition with other existing reactions such as reduction of sulphate ion, the importance of which increases with concentration of the acid, and the hydrogen evolution reaction. The importance of these two reactions are, however, correlated with the above characteristics of the acid.

One should also consider the changes with the composition of the solution of the Gibbs energy of solvation for the several ionic species, including sulphate ions, and a relation might exist with the dilution energy of the sulphuric acid solutions. Indeed, a recent study [3] shows that, for about the same concentration of sulphuric acid, the enthalpy of dilution exhibits wide variation.

4. Conclusion

Although electrodeposition of aluminium from aqueous sulphate solutions has been achieved under very restricted conditions of composition of the electrolyte, it does not appear that these results could lead to fabrication of a negative electrode suitable for use in secondary batteries. Indeed, cadmium ions must be present in the solution leading to codeposition of the two metals. Faradaic yields decrease when the percentage of aluminium in the deposit increases and the hydrogen evolution reaction is predominant in the conditions for which the highest percentage aluminium and Faradaic yield for the aluminium electrodeposition are obtained. However, it may be assumed that slightly different conditions will bring in the desired properties, further studies will be needed to achieve the desired goal.

Acknowledgements

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References

[1] A. Coenders, German Patent 1934 143, dep. 5, VII. 1969.
[2] R. Haase, P. F. Sauermann and K. H. Ducker, *Z. Phys. Chem. NF* 48 (1966) 206.
[3] Y. C. Wu and T. F. Young, *J. Res. Nat. Bur. Stand.* 85 (1980) 11.