JOURNAL OF APPLIED ELECTROCHEMISTRY 2 (1972) 353–354

TECHNICAL NOTE

Electrochemical performance of boron carbide electrodes

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Received 25 July 1972

Two recent publications [1, 2] have described the application of boron carbide as a working electrode in electrochemical studies of, especially, certain platinum metals. However, towards the end of the investigations it was noted [2] that the performance of the electrodes had deteriorated in terms of reproducibility as well as polarographic and potentiometric applicability. This manifested itself in the form of markedly sloping residual current curves and apparently irreversible waves in polarography, and poor response in potentiometry. A purely surface effect was suspected and this was supported by erratic variations of resistance during the course of a polarographic scan, by the variable and relatively high capacitances (0·5→15 nF) measured on electrodes that displayed poor performance, and by the worsening of apparent irreversibility as the scan rate was increased. The cause of the deterioration was sought in treatment changes that inadvertently occurred during the period of the investigations previously reported. Evidently both polishing lap material and polishing paste had been changed during this time and it was soon shown that a powerful surface active agent was contained in the (presently used) laps which are made of material supplied under the name 'Metron B', and that the polishing pastes (Dialap Compound 1/4-1μ) contained a slightly deleterious component; it seems that additives in certain plastics are also active in this way. The effects of all these could be reduced by thoroughly washing in petroleum ether, benzene and chloroform and by boiling the electrodes in concentrated nitric acid; deliberately added surface active agents, ionic and non-ionic, had no effect or caused slight but insufficient improvement. In any case the treatments had no permanent effect, although the improvement was paralleled by slightly reduced capacitances and steadier resistances.

As it was suspected that later specimens of boron carbide were carbon-deficient in the surface layers and that prolonged anodic treatment made the effects worse, it was reasoned that treatments designed to decrease the boron or increase the carbon contents at the surface would provide more permanent improvement. Heating in reducing gases and in chlorine in the temperature range 400–800°C was inconvenient and provided no complete cure. However, an effective procedure that both cleaned and conditioned the surface was found in first stringently cleaning the whole electrode system and then forcing the electrode discs, rapidly rotating in a vertical drill, into pure graphite until appreciable frictional heat was developed. If the electrode was still unsatisfactory, as also evidenced by a high capacitance, a wash in a dilute nitric acid-hydrofluoric acid—Teepol mixture (33+5+2 volumes respectively made up to 100 ml with water) and a firm wiping on moist hardened filter paper to remove excess and loose carbon often completed the activation process. Extensive tests following this treatment particularly on the Ir(IV)→Ir(III), Pd(II)→Pd° and Fe(III)→Fe(II) reductions especially in 0·1M perchloric acid, showed it to be successful and reasonably permanent. The improvement was found to be repeatable. Resistances became reproducible, capacitances fell to 0·1→0·3 nF on 1cm diameter circular electrodes and times of response to changes of potential were shortened. Occasionally it was necessary to repeat a scan before satisfactory results were obtained but, at worst, the residual current curve served as a reference datum for measurements on the polarographic waves. It may well be that that higher capacitances are connected with a thick and firmly adsorbed layer on the electrode surface and that this causes the lengthy response times which in turn lead to apparent irreversibility. Work is continuing in applying the recovered electrodes in electrochemical studies of ruthenium and osmium.

References

[1] E. Jackson and D. A. Pantony, *J. Appl. Electrochem.*, **1** (1971) 113.
[2] E. Jackson and D. A. Pantony, *J. Appl. Electrochem.*, **1** (1971) 283.