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Electrolytic durability of glassy carbon

Graphite carbon is widely used as a cheap and relatively durable electrode material for batteries and in the processes of electrolytic industry [1]. Glassy carbon (GC), a special amorphous carbon modification [2], prepared by slow pyrolysis of certain polymer materials, has proved to be suitable for many applications in electroanalytical chemistry [3] and other electrochemical studies [4]. To elucidate the suitability of GC for electrodes in electrolysis we performed this study where the durabilities of various GC and graphite electrodes were compared in a prolonged electrolysis of aqueous solutions.

Round rods of GC (diameter 8 mm) were prepared with a pyrolytic method described earlier [5]. Three different carbonization temperatures, 800, 900 and 1000° C, were used. The electrical resistivities of the products were 3.9, 0.75, and 0.26 mΩ m, respectively, which correspond well with the values reported in the literature [2]. GC pieces of this size are porous. During 1 month's soaking in distilled water, the weights of a few sample pieces increased by 18 to 31%. The pores were, however, very small; their diameters were about 30 nm as measured from SEM photographs. Non-porous GC electrodes were made by cutting rectangular rods with a diamond saw from commercial GC discs (manufactured by Atomergic Chemetals Corp, New York, USA, and an unknown manufacturer in USSR). The graphite electrodes were synthetic battery electrodes, 8 mm x 57 mm, manufactured by Dae Han Carbon Co, Ltd, Korea.

In the electrolytic runs 1 N hydrochloric acid, sulphuric acid, sodium chloride, and sodium hydroxide solutions prepared from analytical grade reagents were used. Sixteen plastic electrolytic vessels were connected in series and a voltage of 2.8 V was applied between each electrode pair. This caused the evolution of hydrogen, oxygen and chlorine gasses and produced a steady state current of 30 mA (about 10 A m^{-2}). At proper intervals the electrodes were removed, washed, dried, and weighed. At the same time the solutions were replaced with fresh ones.

The results of our experiments are presented in Table I. The carbon electrodes exhibit good cathodic durability except for the porous GC electrodes in the solutions containing sodium ions. They then became brittle and crumbled either in the solutions or during the drying before weighing. This interesting phenomenon resembles the attact (intercalation) of gaseous alkali metals [2] which even causes explosions of samples. The effect may now be due to the sodium metal reduced in the pores of the samples. As anodes, the carbon electrodes were poor, regardless of

TABLE I Electrolytic durabilities of various carbon electrodes

Electrode material	Solution, electrode and evolved gas							
	HCl		H_2SO_4		NaCl		NaOH	
	$\overset{-}{H_2}$	$\overset{+}{Cl_2}$	$\overset{-}{H_2}$	$\overset{+}{O_2}$	$\overset{-}{H_2}$	$\overset{+}{Cl_2}$	$\overset{-}{H_2}$	$\overset{+}{O_2}$
GC (800° C)	G	B	G	B	M	B	B	B
GC (900° C)	G	B	G	B	B	B	B	B
GC (1000° C)	G	B	G	B	B	B	B	B
GC non-porous	G	B	G	B	G	M	G	B
Graphite	G	B	G	B	G	M	G	M

The durabilities are marked with the following notations:
B = bad: significant weight loss (over 2%) in 50 h electrolysis;
M = medium: significant weight loss in 500 h electrolysis;
G = good: no significant weight loss in 500h electrolysis.

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whether oxygen or chlorine was evolved. Acidic solutions, especially sulphuric acid, attacked strongly: the graphite and non-porous GC electrodes were worn by etching, but the porous GC electrodes were crumbled into pieces, in many cases during the first electrolysis day. The durability of all electrodes in alkaline solutions was markedly better.

From our experiments we conclude that in electrolytic durability, non-porous glassy carbon is as good as or, because of its good mechanical properties, in some cases even better than graphite. However, pores make the durability of glassy carbon distinctly worse.

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Fourier transform–infra-red spectra of phosphate coatings on Armco iron

The commercial application of phosphate coatings for protecting metal surfaces has steadily increased [1], but their chemical composition and structure are not yet fully understood [2]. The development of interferometric absorption–reflection techniques has in recent years, greatly improved the possibilities of utilization of infra-red spectroscopy for the study of thin coatings on metal surfaces [3, 4].

Absorption-reflection spectra of phosphate coatings on Armco iron were recorded in the range 400 to 3800 cm^{-1} with a FTS-14V Digilab Fourier Transform Spectrometer, using a Harrick reflectance attachment. The angle between sample plate and light beam was 30°. The measurement parameters were: resolution 4 cm^{-1}, sampling interval 1, number of scans 100. The Fourier transform was calculated with double precision, using 32-bit words. Thin phosphate coatings can be formed by application of phosphoric acid solution alone, i.e. not containing metallic phosphates, to an iron surface.

Fig. 1a shows the spectrum of coatings obtained using H_3PO_4 0.1 N solution at 25° C. This spectrum corresponds to iron phosphate [5]: its structure does not depend significantly on the time of immersion.

The spectra are more complicated for coatings obtained using zinc phosphating solutions, which are mostly employed. Fig. 1b and c show typical spectra obtained for different times of immersion in a standard solution (H_3PO_4 68.7 g + H_2O 41.7 g + ZnO 15.0 g; diluted before use as follows: solution 8 cm^3, H_2O 90 cm^3, 20% $NaNO_2$ 2 cm^3) at 25° C. There is an evident evolution of the spectra, whose main features will be briefly discussed.

At the very first stage of reaction, the spectrum looks similar to that of Fig. 1a. Iron phosphate is, therefore, also formed first in zinc phosphating solution. With increasing time of immersion (Fig. 1b), a progressive splitting of bands corresponding both to $\nu_3(F_2)$ P–O stretching vibrations