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Corrosion behaviour of copper-reinforced carbon electrodes in dilute hydrochloric acid solutions

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The corrosion behaviour of experimentally prepared copper-reinforced carbon electrodes in dilute hydrochloric acid is investigated. The electrodes are not only directly attacked by the acid, but they are also subjected to galvanic corrosion. The baking temperature and time are the most crucial processing variables. A minimum in the corrosion rate is always achieved when the electrodes are baked at 400 °C for 1.5 h, the level depending on the copper content. The corrosion resistance increases progressively with the baking temperature as long as the baking time is less than 1.5 h. Baking for more than 1.5 h results in increasing corrosion rate. The presence of copper increases the corrosion resistance of the prepared electrodes.

1. Introduction

The carbon electrode is the electrode most frequently used in the electrochemical cells. Its preparations, properties and behaviour have been thoroughly investigated [1–9]. The carbon used for the electrode fabrication ranges from glassy carbon to graphite powder [1]. Vacuum-tight vitreous carbon electrodes are used for electrochemical studies in highly corrosive systems where metal electrodes cannot be used [2]. Teflon-bonded carbon electrodes catalysed with highly dispersed platinum metal have been developed for oxygen reduction in H_2SO_4 [3]. Chemical modification of the carbon and graphite electrodes [4] and their protection from oxidation with either a protective coating or surface treatment [5–7] have been found to improve the effectiveness of the electrodes. Panzer [8] used cyclic voltammetry to investigate the behaviour of carbon electrodes in aqueous and non-aqueous systems. Furthermore, Perekherst *et al.* [9] investigated the corrosion resistance of graphite carbon electrodes in dilute sulphuric acid solutions. Nevertheless, carbon electrodes are fragile and mechanically inferior to metal electrodes. They are prone to erosion due to sputtering; they are also prone to cavitation erosion in the bubble collapse and breakdown when using arc discharge in liquids [10]. Such defects may be alleviated by copper reinforcement. For instance, the addition of copper to metal–glass materials improves their strength characteristics [11]. Therefore, the addition of copper to the carbon electrode will, definitely, affect other physical properties such as the electrical and thermal conductivities, and chemical properties such as corrosion resistance.

This paper is one of a series of publications [12, 13] dealing with the preparation, properties and behaviour of carbon/copper composite electrodes. The present study is addressed to reporting and analysing the relationship between the corrosion resistance and the processing variables of the copper-reinforced carbon electrodes (CRCE) in dilute hydrochloric acid solutions.

2. Experimental procedure

2.1. Electrode preparation

The main steps followed for the preparation of the composite electrodes were in the spirit of the procedure usually followed to produce carbon and graphite electrodes [14]. The materials used for the electrode preparation were: Prolabo carbon powder (animal charcoal), 95 μm with a specific gravity of 1.9; 1103-00 Koch-Light pure copper powder, 60 μm with a specific gravity of 8.92, and epoxy resin with a specific gravity of 1.4.

Various carbon/copper mixtures were weighed out and the correct proportions of epoxy resin (as a binder) were added so that the copper content varied from 15%–50%. Each mixture was then hydraulically cold-pressed within a smooth, high finish carbon steel mould for 1 min. A series of loads ranging from 5–20 t were applied. The resulting, disc-like (50 mm × 5 mm) compacts were then baked in a muffle furnace at different temperatures (300–500 °C) for different periods of time (0.5–2.5 h). Subsequently, the compacts were left to cool slowly in a dry atmosphere to reduce thermal strains that may result from a fast and/or uneven cooling. The corrosion rate was then measured in hydrochloric acid solutions of varying concentrations (0.5–2 M).

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2.2. Corrosion tests

A good surface finish was first obtained using a fine emery paper (French-Hubert 000). The surface was then carefully washed with water followed by ether then dried at 105 °C for 30 min. The dimensions of the compacts were then carefully measured with a caliper. To avoid any appreciable change in the corrosiveness of the acid solutions, the compacts were immersed in about 1000 cm^3. They were supported by glass rods having triangular bases with glass pins at each triangle apex. Such compact supports were utilized in order to maximize the free contact of the compacts with the acid solution. After 18 h exposure, the compacts were cold-washed with water followed by acetone, dried at 105 °C and weighed to the nearest milligram. The corrosion rate was obtained from the loss in weight (before immersion and after drying), the original surface area and the exposure time. The total surface area was taken as $\pi D^2/2 + t\pi D$, where D and t are the compact diameter and thickness, respectively. The corrosion rate is reported as milligrams per square decimetre per day (mg dm^{-2} day^{-1}). All the corrosion tests were conducted at 25 °C ($\pm$ 2 °C). The solutions were covered with clock glasses during testing and no particular measures were taken to reduce the access of the atmosphere to them. It is pertinent to point out that the results quoted are the results of single samples.

3. Results and discussion

3.1. General corrosion features

The electrodes were found to be more dense and coherent following the heat-treatment step. Copper agglomeration was easily detected in compacts of copper content $\geq 25\%$ baked at temperatures ≥ 400 °C. Such an observation is merely an indication that the compacts have been sintered at these temperatures. In all cases, however, the surface of the compacts was covered by a thin film of bubbles upon immersion in the test solutions. The number of bubbles being higher in compacts of higher copper content, those pressed at lower compacting pressures and baked at lower temperatures for shorter periods of time. After the compacts have been reweighed, those with copper content $\geq 25\%$ possessed a very rough green surface, indicating that preferential attack has occurred with the separation of cupric salts. No pits were found to occur at the contact points between the compacts and the supporting glass pins. On the other hand, CRCEs with 15% Cu had a very smooth black surface with a higher reduction in their thickness; they were homogeneously attacked by the test solution.

The thin bubble layer was formed as a result of the penetration of the solution into the voids of the compacts and the consequent release of entrapped air. The green rough deposit is a layer of cupric chloride which resulted from the chemical reaction between cupric oxide and dilute hydrochloric acid. Cupric oxide usually forms when copper is heated in air in the vicinity of 300 °C [15]; the heat-treatment conditions obviously favour the formation of cupric oxide. Cuprous oxide might also have been formed (at higher temperatures) which, in turn, reacts with hydrochloric acid forming white cuprous chloride and, in the presence of air bubbles, is gradually turned green due to the formation of basic cupric chloride. Direct attack of the copper is not likely to occur under these circumstances, particularly as the acid solution is not concentrated and the corrosion tests were conducted at ambient temperature. More importantly, galvanic corrosion is taking place because of the presence of carbon and copper in contact within the hydrochloric acid solution. The copper, being less noble, is subjected to dissolution and the electrochemical reactions taking place in the galvanic cell, Cu/HCl/C, may be summarized as follows

$$\text{anodic reaction: } Cu = Cu^{2+} + 2e \text{ (oxidation)}$$

$$\text{cathodic reaction: } O_2 + 4H^+ + 4e = 2H_2O \text{ (reduction)}$$

Therefore, the compacts are not only directly attacked by the acid solution, but they are also subjected to electrochemical reactions. The latter being governed by the former, in the sense that upon vigorous direct attack, a stagnant bubble layer forms on the surface with subsequent cupric salt separation; the result is a decrease in the rate of electrochemical reactions and eventually the overall rate of corrosion is suppressed as will be discussed later.

3.2. Quantitative analysis of the results

The most striking feature is the greater corrosion resistance of CRCEs with higher copper content. A typical behaviour is shown in Fig. 1 for a CRCE with 1% epoxy resin, compacted at 5 MPa baked for 1.5 h at 400 °C and tested in 0.1 M HCl: the corrosion rate decreased by about one order of magnitude as the copper content increased from 15% to 50%. Upon copper addition, the tendency for oxide formation increases and consequently, direct chemical attack is favoured over the galvanic action as discussed above.

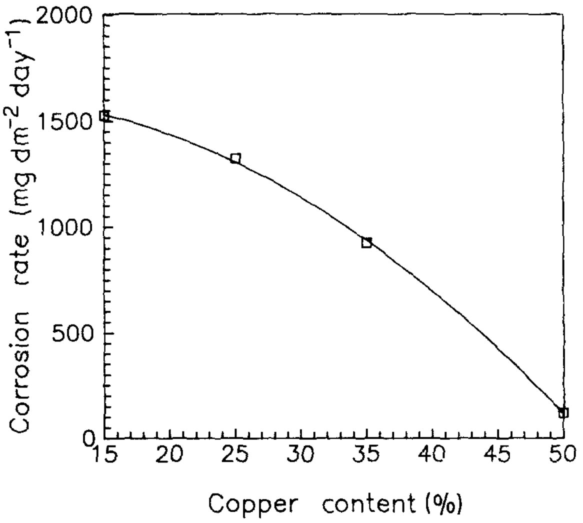

Figure 1 Variation of the corrosion resistance of the CRCEs with copper content. Baking time 1.5 h, compacting pressure 5 MPa, baking temperature 400 °C, 1% epoxy resin, acid concentration 0.1 M.

This explains the previous observation, that compacts of higher copper content possess a rougher green surface. The 1.5 h baking time is critical. For instance, as shown in Fig. 2, the rate of corrosion decreases for compacts of 25% Cu, 1% epoxy resin, pressed at 5 MPa when baked at 400 °C, as the baking time varies from 0.5–1.5 h and in contrast the rate increases upon baking for more than 1.5 h. The variation of the corrosion rate with the baking temperature is similar to that with the baking time. Fig. 3 typically depicts such a behaviour, with the highest corrosion resistance observed for compacts baked at 400 °C. Apparently, the influence of the baking time and temperature is mutual and prolonged heating is equivalent to baking at higher temperatures (see Figs 2 and 3). The primary increase in the corrosion resistance with the baking temperature is a consequence of the early softening and flow of the epoxy resin accompanied by the expansion of the entrapped air in the compacts, which in turn causes an increase in the proportion of void spaces. Intuitively, upon immersion in the test solution, the entrapped air is expelled, due to the acid penetration, and accumulates in the form of the previously mentioned bubble layer. This stagnant layer reduces the rate of the mass transfer step occurring during the electrochemical reaction, discussed earlier, and catalyses the direct chemical attack. The net result is a decrease in the rate of corrosion because of the hindered diffusion in the electrolytic solution. On the other hand, upon further increase in the baking temperature, the resin is subjected to thermal decomposition, followed by charing and finally is driven off, leaving micro-voids behind. The mobility of the particles is simultaneously increased and diffusion occurs at their interfaces, whereby the forces of surface tension now become effective in reducing the voidage of the compact mass. The net result is a sintered compact mass obtained by the coalescence of the powder particles accompanied by grain growth. When immersed in the test solution, such compacts will be attacked easier than their counterparts baked below 400 °C. The galvanic action is now favoured leading to the observed increase in the corrosion rate above 400 °C, as seen in Fig. 3. Accordingly, if we compare Figs 2 and 3, we can simply state that baking the electrode for a shorter period at 400 °C is equivalent to baking the electrode for 1.5 h at a lower temperature; the reverse is also true.

Fig. 4 shows the variation of the corrosion rate of CRCEs of different copper content with the baking temperature when tested in 0.1 M HCl. Obviously no minimum in the corrosion rate is observed; instead, regardless of the copper content, there is a tendency for increasing the corrosion resistance of the CRCEs with increasing the baking temperature. Such a behaviour is expected because the baking time is 1 h: sintering is not likely to take place and entrapped air is expelled from void spaces (upon immersion in the test solution) leading to the formation of the bubble layer and eventually increasing the corrosion resistance as discussed earlier. This is not truly the case, however,

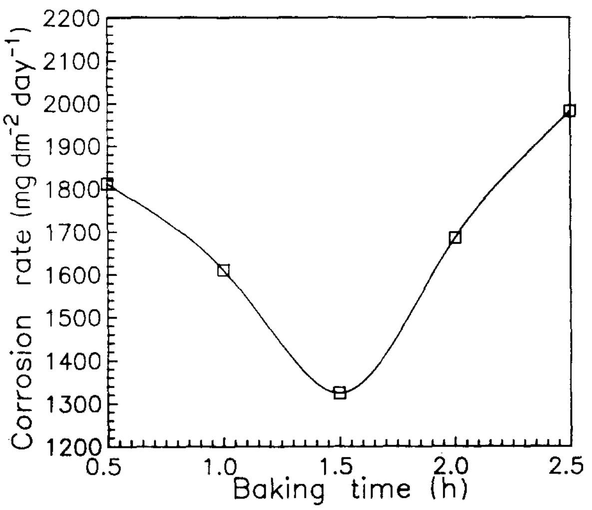

Figure 2 Dependence of the corrosion rate for the CRCEs on the baking time. Compacting pressure 5 MPa, 25% Cu, baking temperature 400 °C, 1% epoxy resin, acid concentration 0.1 M.

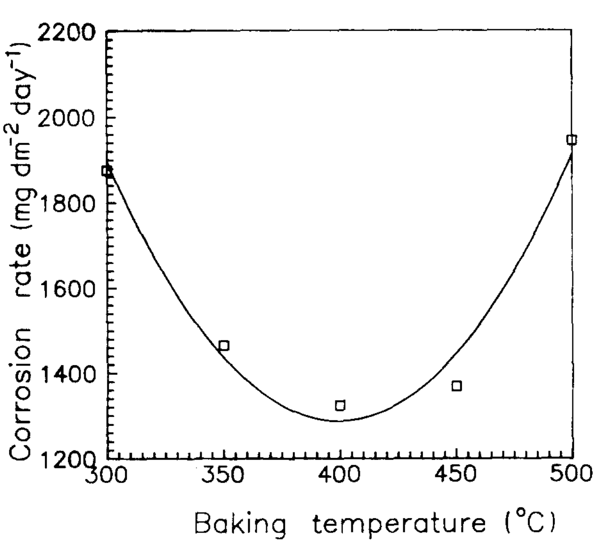

Figure 3 Variation of the corrosion rate of the CRCEs with the baking temperature. Baking time 1.5 h, 25% Cu, compacting pressure 5 MPa, 1% epoxy resin, acid concentration 0.1 M.

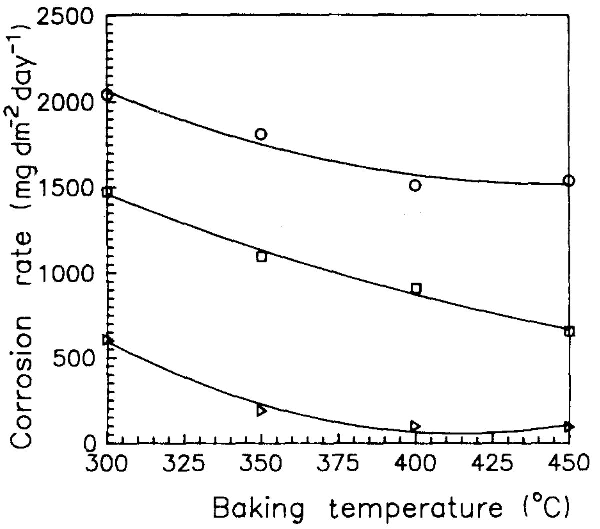

Figure 4 Effect of the baking temperature on the corrosion resistance of compacts with different copper contents baked for 1 h. Compacting pressure 5 MPa, 1% epoxy resin and tested in 0.1 M HCl. Copper content: (○) 15%, (□) 35%, (△) 50%.

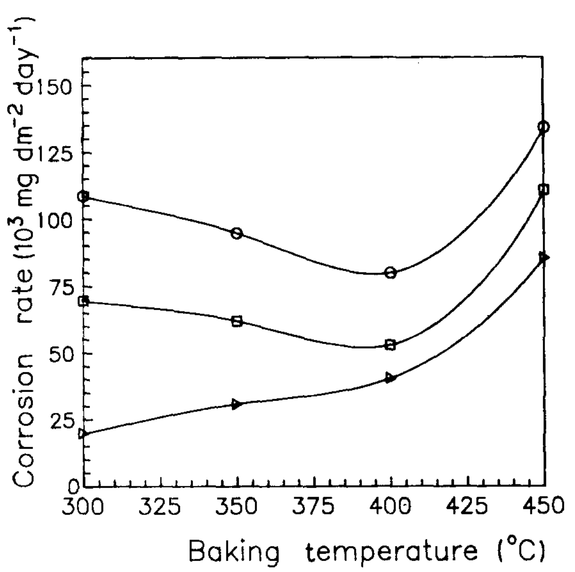

Figure 5 Effect of the baking temperature on the corrosion behaviour of compacts with different copper contents baked for 1.5 h. Compacting pressure 5 MPa, 1% epoxy resin and tested in 1.0 M HCl. Copper content: (○) 15%, (□) 35%, (△) 50%.

when the baking time is 1.5 h as seen from Fig. 5. Nonetheless, as the copper content increases, the corrosion resistance increases, in spite of using 1 M HCl. But at a given copper content, the corrosion rate is basically increasing as the baking temperature varies from 300–450 °C, the change being highest for the CRCE of 50% Cu. Obviously, the sintering operation is taking part in accelerating the corrosion rate. For the 15% and 35% CRCEs this is not the case below 400 °C, and we observe a similar trend to that of Fig. 3, which describes the behaviour of compacts containing 25% Cu. Such behaviour is as expected, because we are baking for the criticial period of 1.5 h. These compacts would exhibit higher void space content leading to the observed corrosion behaviour. On the other hand, when baked for 2 h, sintering occurs and the corrosion rate increases with the baking temperature, as seen from Fig. 6. One can easily check the opposing effect of the baking temperature on CRCEs baked for two different periods of time bracketing the critical 1.5 h baking period: i.e. 1 h and 2 h; see Figs 4 and 6. Furthermore, the effect of the baking temperature is suppressed when baking for 2 h, because increasing the baking temperature is not greatly enhancing the corrosion rate as seen from Fig. 6. The elevation of the compacting pressure will enhance the intimacy of contact within the powder mix, leading to increasing areas of contact by eliminating voids and expelling air or any entrapped gases. The rate of acid penetration will, therefore, be reduced and we will end up with a more corrosion resistant compact mass. Fig. 7 depicts this behaviour. Furthermore, the previously discussed relationship between the baking temperature and the rate of corrosion for compacts of $\leq 35\%$ (see Figs 3 and 5) still holds regardless of the compacting pressure, as shown in Fig. 8.

The acid concentration strongly influences the corrosion rate of the compacts: the rate increases

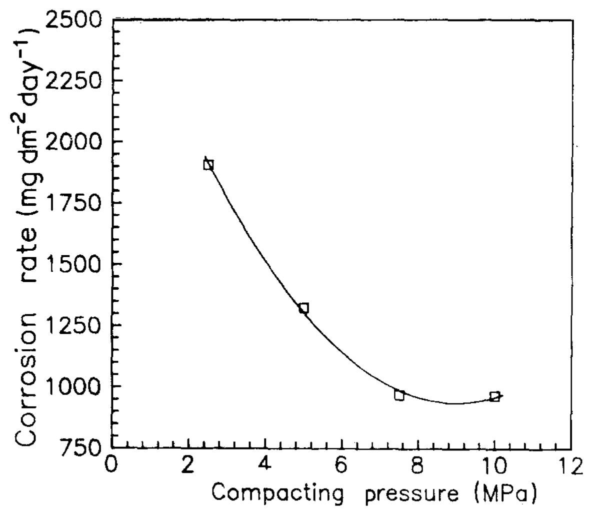

Figure 7 Corrosion resistance versus compacting pressure. Baking time 1.5 h, 25% C, baking temperature 400 °C, 1% epoxy resin, acid concentration 0.1 M.

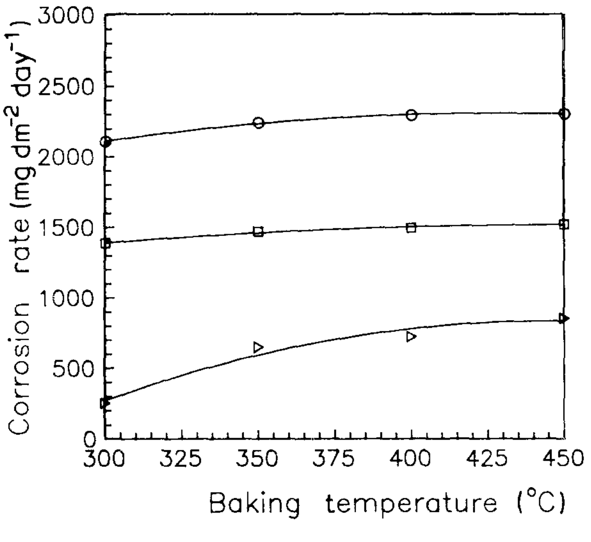

Figure 6 Effect of the baking temperature on the corrosion rate of compacts with different copper content baked for 2.0 h. Compacting pressure 5 MPa, 1% epoxy resin and tested in 0.1 M HCl. Copper content: (○) 15%, (□) 35%, (▽) 50%.

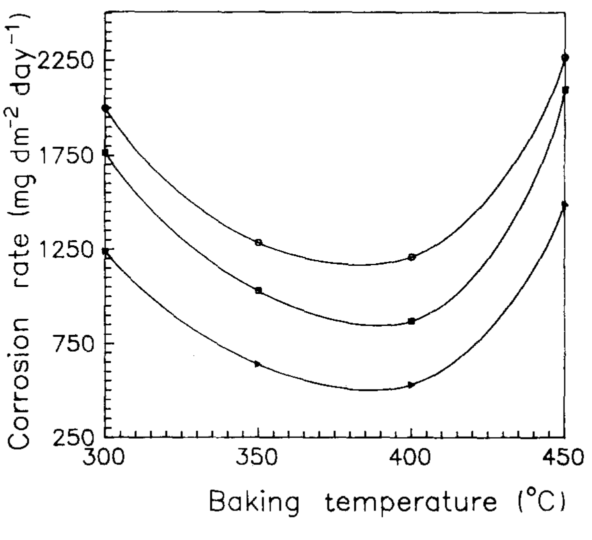

Figure 8 Variation of the corrosion behaviour with the baking temperature for electrodes compacted at different pressures. 35% Cu, 1% epoxy resin, baking time = 1.5 h, tested in 0.1 M HCl. Compacting pressure (MPa): (○) 2.5, (□) 7.5, (▽) 10.

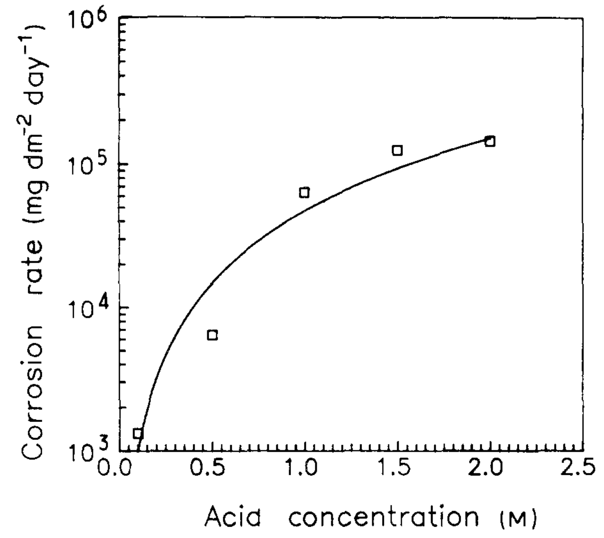

Figure 9 Corrosion rate versus molarity of hydrochloric acid. Baking time 1.5 h, 25% Cu, baking temperature 400 °C, 1% epoxy resin, compacting pressure 5 MPa.

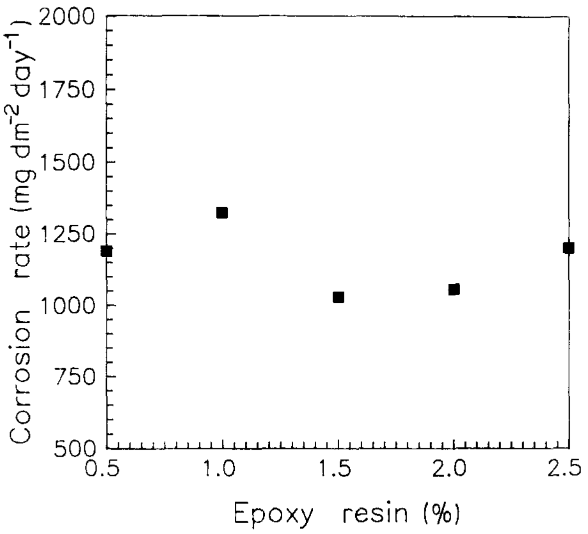

Figure 10 Corrosion rate versus epoxy resin content. Baking time 1.5 h, 25% Cu, baking temperature 400 °C, acid concentration 0.1 M, compacting pressure 5 MPa.

about two orders of magnitude if the acid concentration increases from 0.1 to 2.0 M, as shown in Fig. 9 for compacts of 25% Cu, 1% epoxy resin, pressed at 5 MPa and baked at 400 °C for 1.5 h. On the other hand, Fig. 10 shows that the variation of the epoxy resin content has no major effect on the corrosion behaviour of the CRCEs.

4. Conclusions

Attempts have been made to achieve some understanding of the relationship between the corrosion resistance of the electrodes and their processing parameters. The foregoing analysis leads to the following conclusions.

1. Copper agglomeration and elimination of void spaces occur above 400 °C, when the electrodes are baked for 1.5 h or more; sintering is likely to take place under these conditions.

2. The CRCEs are subjected to direct chemical attack and galvanic corrosion. Sintering favours galvanic corrosion.

3. The baking time and temperature are the most crucial experimental variables. A minimum corrosion rate is observed when baking at 400 °C for 1.5 h, depending on the copper content.

4. The CRCEs show an increase in the corrosion resistance as the baking temperature increases as long as the baking time is less than 1.5 h. The reverse is true when baking for more than 1.5 h.

5. The progressive increase of the copper content and/or compacting pressure increases the corrosion resistance as long as the baking time and temperature are held constant.

6. The acid concentration increase enhances the corrosion rate, while the variation of the epoxy resin content has no major influence.

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