Journal of Power Sources, 6 (1981) 185 - 192

INVESTIGATION OF CARBON–TEFLON PLAQUE RESISTIVITIES

B. G. DEMCZYK and C. T. LIU

Westinghouse Electric Corporation, Research and Development Center, Pittsburgh, PA 15235 (U.S.A.)

(Received June 25, 1980; in revised form September 20, 1980)

Summary

The resistivities of pressed carbon plaques containing varying amounts of Teflon binder were measured *via* a d.c. resistance bridge arrangement. Correlation of the resistivities of samples with such factors as sample thickness, density, Teflon content, and presence of dispersion agent was investigated. Results indicate an inverse relation between resistivity and plaque thickness for thicknesses up to 6.35 mm, little correlation of apparent density with plaque resistivity, and a dominant dispersion agent effect in the range of Teflon plaque loadings normally employed in air electrode fabrication. The above results provide physical insight into electron conduction within pressed carbon–air electrodes. Results of these experiments are discussed.

Introduction

Carbon powder is utilized in the air electrode structure to provide a high surface area for oxygen adsorption and electrolyte penetration. It is essential that this material facilitates electron conduction so that the electrochemical reactions

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

and

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$$

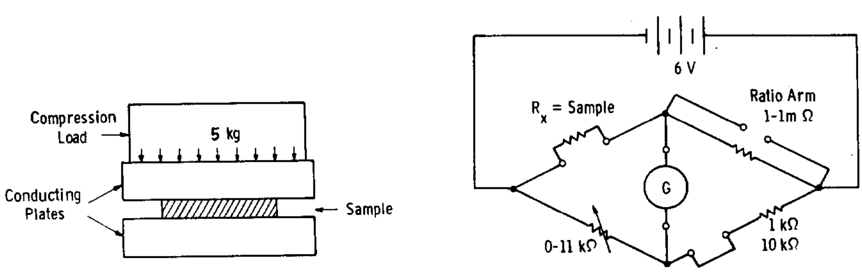
can freely occur. Since carbon is a semiconducting material [1], it offers a resistance to this process. The carbon black powder, as used, is a compressible material, and its electrical properties are, in general, complicated. Previous studies [2, 3] of compressed carbon powders point to a resistivity dependence on such factors as particle size, applied external pressure, speed of application of this pressure, and frequency of the measuring current (skin effect). Further complications arise when one introduces an impurity (Teflon, PTFE dispersion) into the system. Teflon is incorporated into air electrode materials to provide structural integrity to the carbon matrix as well as imparting necessary hydrophobic characteristics. These studies have centered on the correlation of the resistivities of pressed carbon–Teflon plaques with such factors as plaque thickness, Teflon particle content, and presence of Teflon particle dispersion agent*. The particular carbon black under investigation (Shawinigan acetylene black), formed via thermal decomposition of acetylene gas, has properties which approach those of finely divided graphite (mean particle size: 420 Å). Added to the above was a tetrafluoroethylene in non-ionic surfactant dispersion (Teflon 30B TFE resin dispersion), having a particle size range of 0.05 - 0.5 μm.

Procedure

Samples were prepared by loading incremental masses of dry carbon–Teflon mixtures into a 10 cm^2 stainless steel die and cold pressing into plaques at 17.24 MPa. These plaques were then thickness measured and their resistance determined *via* a d.c. Wheatstone bridge arrangement under a compressive load of 5 kg (Fig. 1(a)). Resistances were converted to resistivity values *via* the relation:

$$\rho = \frac{RA}{t} \times \text{units conversion factor}$$

where R = resistance (Ω), t = plaque thickness (mm), A = plaque area = 10 cm^2, ρ = resistivity (Ω cm). The above procedure largely eliminates local pressure differentials within the samples, which has plagued compressed carbon powder measurements in the past. In addition, resistance variation with source current frequency is eliminated since we are dealing in d.c. measurements.



(a) (b)

Fig. 1. (a) Plaque pressing configuration; (b) schematic of resistance measuring circuit. Range 1 mΩ - 11 mΩ.

---

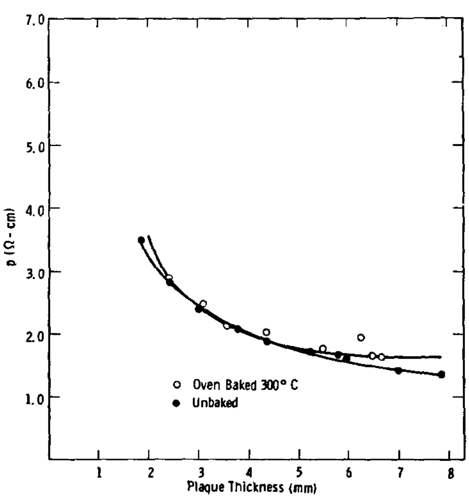
*Dispersion agent is decomposed *via* oven baking — thus we refer to baked and unbaked samples.

Experimental results and discussion

Resistivity vs. *plaque thickness*

For all plaque samples measured, the ρ *vs.* t plots (Figs. 2 - 4) assume the same general shape. This trend is shown for both over-baked and non-baked mixtures, and was essentially independent of Teflon content. Clarification of the ρ *vs.* t curves is obtained by examining a typical t *vs.* m plot (Fig. 5), where m is the mass of the plaque. As shown, the t/m ratio decreases (from 2.54 to 2.06 mm/g for a 30% Teflon loading case) for increased loading in the range 0.5 - 2.75 g. Thus, decreased particle-to-particle contact in the thinner samples accounts for their higher apparent resistivity.

A qualitative explanation of this phenomenon can be ascertained as follows. As previously mentioned, samples were prepared by pressing carbon–Teflon powder mixtures into plaques under high pressure. The above largely duplicates a similar step in air electrode construction. Figure 6(a) depicts a conceptual internal plaque stress distribution within low powder loading samples during this step. As shown, due to close particle proximity in these samples, compressional force components lie primarily in the vertical direction. Upon release of the compression force, elastic restoring forces within the plaque are exerted almost exclusively upon the major plaque faces, causing a thickness increase. However, as material loading is increased, the stress distribution changes to a pattern similar to that of Fig. 6(b) in which non-negligible lateral stress components effectively force carbon–



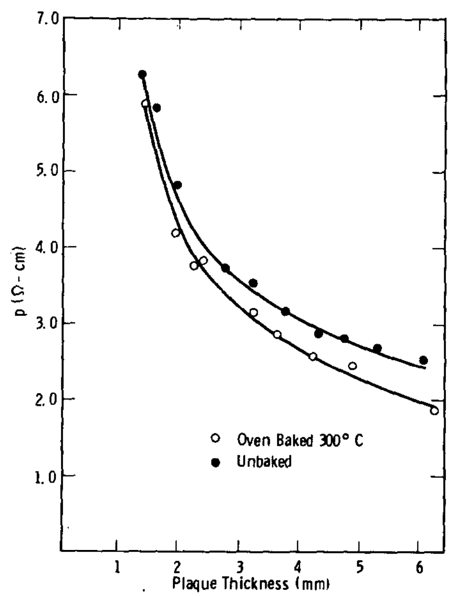
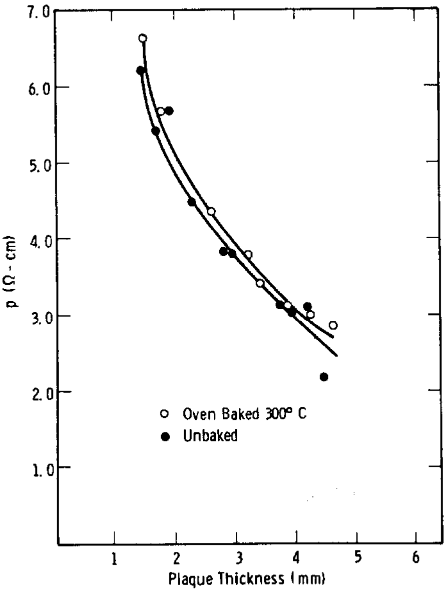


Fig. 2. Resistivity *vs.* plaque thickness (10 wt.% Teflon).

Fig. 3. Resistivity *vs.* plaque thickness (30 wt.% Teflon).



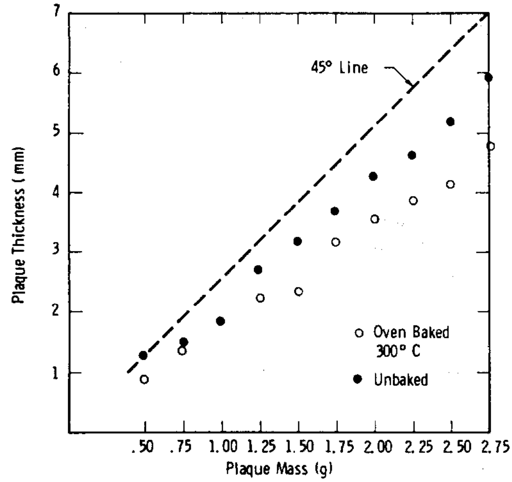
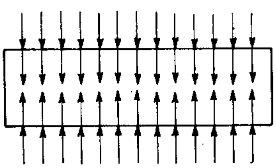
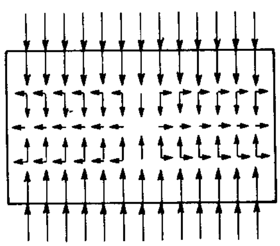


Fig. 4. Resistivity *vs.* plaque thickness (50 wt.% Teflon).

Fig. 5. Plaque thickness *vs.* plaque mass (30 wt.% Teflon).



(a)



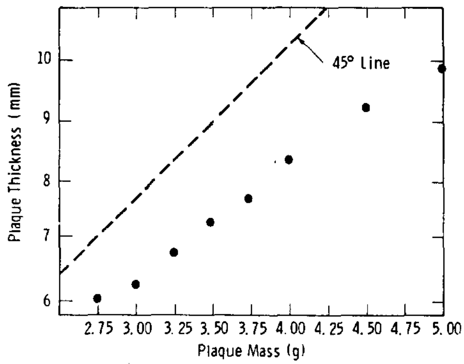
(b)

Fig. 6. (a) Plaque stress distribution — thin sample; (b) plaque stress distribution — thick sample.

Teflon particle aggregates outward from the plaque center (lower resulting density in this region). Therefore, upon release of pressure, internal restoring forces act on all plaque faces, resulting in a smaller proportional post pressing thickness expansion. Thus, we obtain the characteristic t/m plot.

A series of higher powder loading samples yielded the plots of Figs. 7 and 8. As shown, the t/m ratio continues to decrease slightly (to ~0.77) as the slope of the ρ *vs.* t curve approaches zero. This illustrates that the above effects become more pronounced as loading is increased.

Over a range of 15 - 30% Teflon particle content, the oven-baked (wetting agent decomposed) samples exhibited lower resistivities than their unbaked (weight) counterparts. An examination of t *vs.* m curves reveals a closer particle packing in the former samples. Therefore, one may postulate that the dispersion agent acts as a lubricant permitting greater mobility of



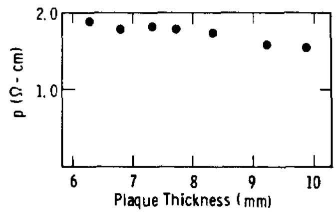


Fig. 7. Plaque thickness *vs.* plaque mass (30 wt.% Teflon).

Fig. 8. Resistivity *vs.* plaque thickness (30 wt.% Teflon).

carbon particle aggregates with respect to one another. Upon release of the pressing dies, the assembled carbon–Teflon plaques with large amounts of wetting agent present, tend to expand more than the "dry" plaques, *i.e.*, "wet" plaques are more compressible, but also less able to retain their compressed dimensions. Outside this range, however, the resistivity of the oven-baked samples exceeds the unbaked plaques. For higher Teflon loadings (> 30%) there remains enough (undecomposed) dispersion agent to promote the above effect.

Correlation with Teflon content

Studies show a direct correlation of resistivity with Teflon content of the (unbaked) carbon plaque material (Fig. 9). As shown, for Teflon loadings below 30% the resistivity of unbaked samples increases with Teflon content. This increase is greater for the thinner samples. In addition to demonstrating the increased dielectric material content within the plaque, this trend also reflects the lower resistance to post-pressing shape change of the higher Teflon content (and higher dispersion agent content) mixtures. Above 30 wt.% Teflon content, however, resistivity decreases with increasing Teflon content, reflecting the increased adhesion between the more populous Teflon particles and/or increased displacement of the smaller Teflon particles within the carbon–Teflon mixture — both result in a smaller average distance between carbon particle aggregates.

The correlation of resistivity with Teflon content for oven-baked samples is more complex. If one examines the ρ *vs.* Teflon wt.% plot for baked samples, one observes the unbaked sample curve shape for loadings above 20%. Therefore, for the higher Teflon loadings, the above wetting agent effect predominates, indicating that a significant quantity of the above has survived the baking process (studies to determine just how much survives are presently in progress). In the smaller loadings, however, little remains and we observe a Teflon particle adhesion effect (*i.e.*, $\rho \propto 1/\text{wt.\% Teflon}$).

Figures 2 - 4 show a general increase in the slope of the ρ *vs.* t curve with increased Teflon content, further illustrating the dielectric effects of

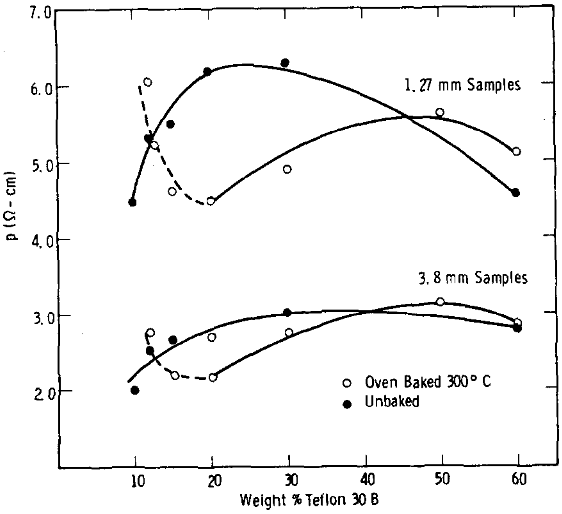


Fig. 9. Resistivity *vs.* Teflon content.

the Teflon particles. Plaques with smaller Teflon loadings are, as a whole, more conductive, since electron conduction paths in these samples offer less resistance than those in higher Teflon content samples. Consequently, for these samples, resistivity dependence on path length is less critical. The above holds for both baked and unbaked particle mixtures.

Resistivity vs. *apparent density*

As Fig. 10 shows, experimental results yielded little relation between plaque apparent density and resistivity. This is in agreement with previous studies of compressed carbon powders [3]. It was found that, for the thicker samples (3.8 mm), resistivity was nearly independent of plaque density over a density range of 0.3 - 0.6 g/cm^3. For these samples, plaque thickness is the resistivity controlling parameter. For the thinner samples (1.27 mm), particle packing effects come into play, the exact nature of which is not clear from the data (nor in previous studies) [3]. Thus, one observes a scatter of data points.

Figure 11 shows the relation of apparent plaque density to Teflon content. As shown, for the 3.8 mm plaque samples, the density generally increases with the plaque Teflon content. Since both the acetylene black and the Teflon particles utilized possess approximately the same intrinsic density (~2.2 g/cm^3) one would initially expect little effect of Teflon content upon plaque density. However, since Teflon particles are, on average, smaller than the carbon particle aggregates, one may predict the tighter packing for higher Teflon content samples that Fig. 11 shows. Also shown is the effect of the dispersion agent — baked samples exhibit higher densities than unbaked samples. This is consistent with the concept of wetting agent "lubrication" previously mentioned. The 1.27 mm samples again yielded scattered data, pointing to non-uniform post pressing plaque expansion in these plaques.

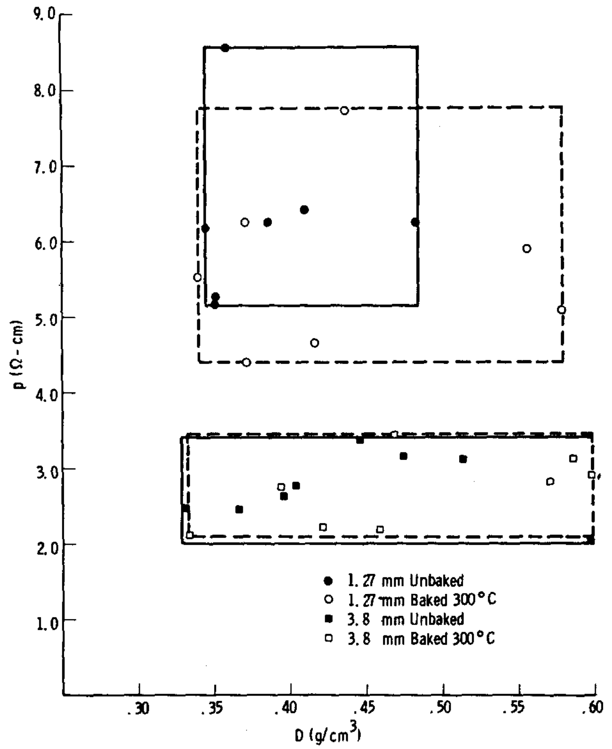


Fig. 10. Resistivity *vs.* plaque density.

Conclusions

It has been shown that the resistivity of compressed carbon–Teflon plaques is reduced for increased plaque thickness up to thicknesses of about 6.35 mm, beyond which the resistivity approaches a constant value (up to 10.16 mm). As discussed in this report, this effect can largely be accounted for by the Teflon plaque (and air electrode) fabrication procedure. Increased Teflon loading enhances the above.

The effects of Teflon dispersion within conductive carbon plaques on their resistivity can be classified into the following areas:

(1) Teflon particle size effect;

(2) dielectric effect of Teflon particles;

(3) adhesive qualities of "wet" Teflon particles;

(4) dispersion agent effect.

Effect (4) has been shown to be the dominant one within a Teflon loading range of 15 - 30 wt.%. Above 30% loading, effects (1) and (3) dominate. Effect (2) appears to be secondary in importance to the above and is strictly a function of the Teflon loading. Therefore, in the loading range typically utilized in air electrode structures, effect (4) is of the most immediate concern, as corroborated by previous studies [4].

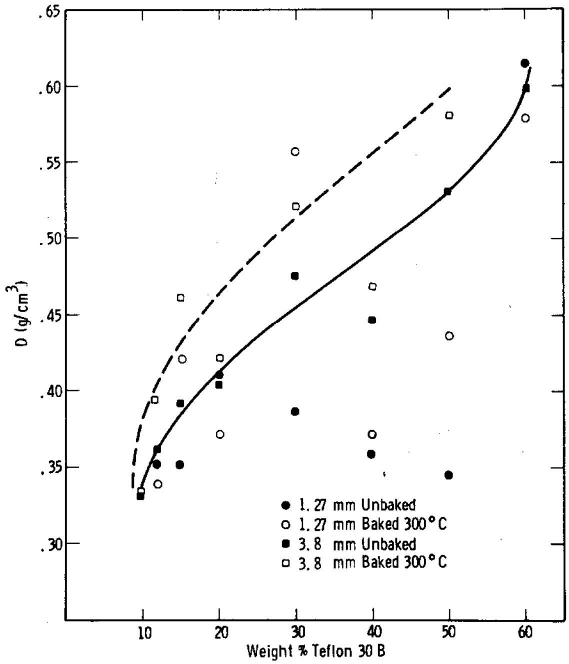


Fig. 11. Plaque density *vs.* Teflon content.

As in previous work, little correlation was found between plaque apparent density and resistivity. There is some indication that increased Teflon content contributes to a higher carbon–Teflon mixture apparent density.

Although resistivities vary with the above factors, the magnitude of these variations is relatively small (all resistivity in the range of 2 - 8 ohm cm), a result that, from the standpoint of electronic conduction, can be used to support the use of higher Teflon loadings in air electrode fabrication.

Acknowledgements

The authors thank Mr. P. R. Gongaware for his valuable assistance in the preparation and measuring of samples. The financial support of the United States Department of Energy is also acknowledged (Contract No. EY-76-C-02-2949,* 000).

References

1 R. E. Nightingale, (ed.), *Nuclear Graphite,* Academic Press, New York, 1962.
2 A. Voet, Electrical conductance of carbon black, *12th Annu. Wire and Cable Symp., Asbury Park, NJ, 1963.*
3 K. J. Euler, The conductivity of compressed powders. A review, *J. Power Sources, 3* (2) (1978) 117.
4 C. T. Liu, Wet proofing of air electrodes for use in alkaline electrolytes, *154th Electrochem. Soc. Fall Meeting, Pittsburgh, PA, 1978.*