SPECIFIC CONDUCTIVITY OF COPPER-REINFORCED CARBON ELECTRODES

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Abstract

A systematic investigation of the effect of adding copper to carbon electrodes has been undertaken. Composites, disc-like carbon-copper electrodes (35 x 5 mm) were prepared with varying percent of binding agent. They were pressed at different compacting pressures followed by sintering at different temperatures for varying periods of time. The specific conductivity of the compacts was investigated.

Sintering temperatures higher than $500^{\circ}C$ are detrimental. The specific conductivity is inversely related to each of the sintering time and temperature. On the other hand, the specific conductivity increases with the carbon to copper ratio and the compacting pressure. Severe limitations are imposed by the utilized sintering atmosphere.

1. Introduction

Composite materials are produced when two or more materials are joined
to give a combination of properties that cannot be attained by each of
the individual materials. The concept of "composites" will be utilized
to investigate the transport, physical and mechanical properties of
carbon electrodes. They are widely used in electrochemical industries
(1), e.g. in the manufacture of primary batteries (cells), in the
production of Chlorine and NaOH by brine electrolysis and in the arc
furnace used to manufacture products such as calcium carbide,
phosphorus and ferrosilicon. Carbon electrodes are mechanically
inferior to metal electrodes as they are brittle and prone to erosion.
Besides, the thermal conductivity of carbon is relatively low. These
defects can be alleviated by copper reinforcement. Copper addition
could affect other properties such as electrical conductivity as well.
This paper forms the first part of a series of publications dealing
with the preparation and the properties of carbon-copper composite
electrodes. We start by observing the transport properties, with
special emphasis on the specific conductivity of the copper-reinforced
carbon electrodes (CRCE). The main purpose of the present paper is to
report and analyze the relationship between the specific conductivity
and the processing variables of the CRCE.

2. Experimental

Pure copper powder and carbon powder were utilized for the preparation
of specimens. Stearic acid was used as a binder (lubricant). The
composites, carbon/copper disc-like, electrodes (35 mm diametere x 5mm
thickness) were obtained by compacting different mixtures of the above
mentioned constituents in a hydraulic press for five minutes followed

by sintering at different temperatures for different periods of time. Finally, the electrical resistance of the CRCE was measured and consequently converted to specific conductivity by the following simple relation:

$$\text{specific conductivity} = \frac{t}{R*A} \; \text{ohm}^{-1} \cdot \text{cm}^{-1}$$

where:

t = thickness of the CRCE, cm

R = electrical resistance of the CRCE, ohm

A = cross sectional area of the CRCE, cm^2

The carbon to copper ratio in the CRCE ranged from 1:1 up to 4:1 whereas for the stearic acid content, it was limited to 2%. The compacting pressure ranged from about 0.5 to 2.0 tons/cm^2. The sintering temperature and time ranged from 400°C to 680°C and from 1 hour to 5 hours respectively. For the sake of comparison, some compacts were entirely prepared from carbon.

Many factors dictated the use of stearic acid. Firstly, as a lubricant in order to reduce the density gradient that may borne through the specimens as a result of compressing the carbon and copper powders. Secondly, as a binder which may help reducing nonhomogeneity resulting from mixing copper and carbon powders. Finally, organic lubricants are known to reduce oxidation of surfaces during the sintering operation (2), which is an expected phenomenon, particularly that sintering was carried out in a muffle furnace, i.e. an oxidizing atmosphere.

3. Results and Discussion

The electrical resistance of the samples sintered at temperature above $500^{\circ}C$ (regardless the C:Cu ratio, sintering time and used pressure) was in the Mohm range, resulting in extremely low specific conductivity as shown in Tables 1,2 and 3. The sharp decrease in specific conductivity is probably due to the oxidation of copper and the formation of copper oxide which is considered to be a semi conductor (3). In addition, carbon is also known to oxidize at $500^{\circ}C$ (4) leaving behind a porous and brittle structure. Therefore the sintering operation was conducted in the range of 400 to $500^{\circ}C$.

Table (1) Specific conductivity of composite carbon electrodes with a carbon to copper ratio of 3:1, Binder=1.5%, P=1.04 ton/sq. cm, time=3hours

Temp. (°C)	400	500	600	680
Conductivity $\Omega^{-1}.cm^{-1}$	$5.4*10^{-3}$	$2.3*10^{-3}$	$1.6*10^{-7}$	$3.55*10^{-8}$

Table (2) Specific conductivity of composite carbon electrodes at 680°C, carbon to copper ratio of 3:1 , Binder=0.5%, P=1.04 ton/sq. cm

Time (hours)	1	2	3	4	5
Conductivity $\Omega^{-1}.cm^{-1}*10^{8}$	4.16	3.12	5.20	4.80	2.60

Table (3) Specific conductivity of composite carbon
electrodes at 680°C, carbon to copper ratio
of 3:1 , P=1.04 ton/sq.cm and time=3hrs

Binder %	0.0	0.5	1.0	1.5	2.0
Conductivity $\Omega^{-1}.cm^{-1}*10^8$	7.80	5.20	3.67	3.55	3.43

Figures 1-3 show that the lower the sintering temperature the higher
the electric conductivity. This may be attributed to the decrease in
the rate of oxidation of the composite constituents at low
temperatures. As the sintering temperature increases from 400 to
500°C, the decrease in the specific conductivity ranges from as low
as 30% up to about one order of magnitude as shown in Figures 1,2 and
3. Figure 1 also indicates that the elevation of the carbon to copper
ratio increases the conductivity. An observation in full agreement
with the mechanics of composite materials (5). The resistivity of
metallic constituents increases with temperature (6), and at a given
temperature, as the carbon content increases, the contribution of the
copper phase to the overall macroscopic properties of the composite
decreases. Consequently, the resistivity of the CRCE is expected to
decrease; a condition amenable to an elevation in the specific
conductivity. Furthermore, the increase in conductivity of CRCE with
increasing carbon to copper ratio in the temperature range of
400-500°C may be attributed to the decrease in the amount of the

weakly conducting copper oxide formed as a result of copper oxidation within the above temperature range. Elevation of carbon content will rise the specific conductivity approaching an upper bound limit of pure carbon electrodes. Tables 4 and 5 show that the specific conductivity of the pure carbon electrode lies in the range of $24*10^{-3}$ to $33.7*10^{-3}$ ohm^{-1} ohm^{-1}. One can then easily verify that increasing the carbon content will eventually coincide to the upper bound limit on the specific conductivity. The overall macroscopic response is dependable on the higher sensitivity of the copper phase to temperature variations when compared to that of the carbon phase. Table 4 shows the variation of the specific conductivity of pure carbon with sintering temperature with a 1% binder composition. One can easily deduce that the variation of the used sintering temperature almost unaffects the conductivity of pure carbon electrodes. $(33.7*10^{-3}$, $35* 10^{-3}$, $31.6*10^{-3}$ ohm^{-1} cm^{-1}: a variation of about 3%).
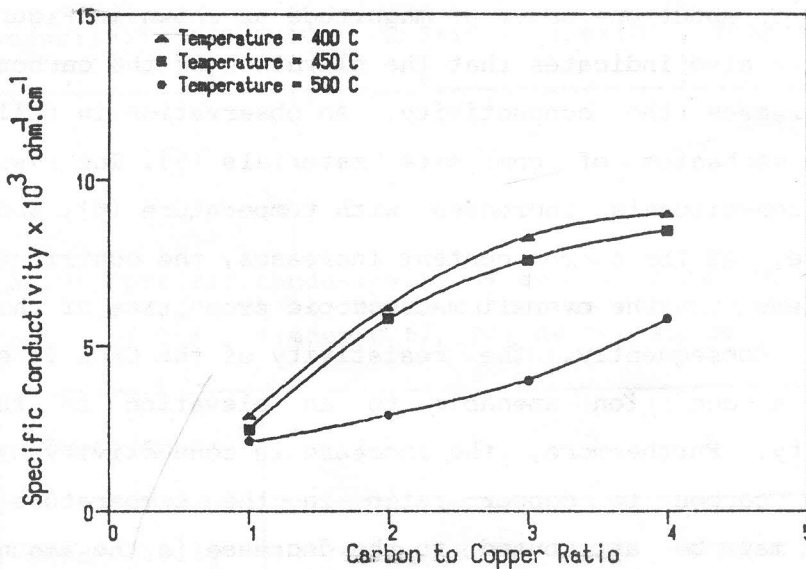

Figure 1: Effect of the carbon to copper ratio and the sintering temperature on the specific conductivity of the CRCE [time=3hrs, P=1.04 ton/sq.cm, binder=1%]
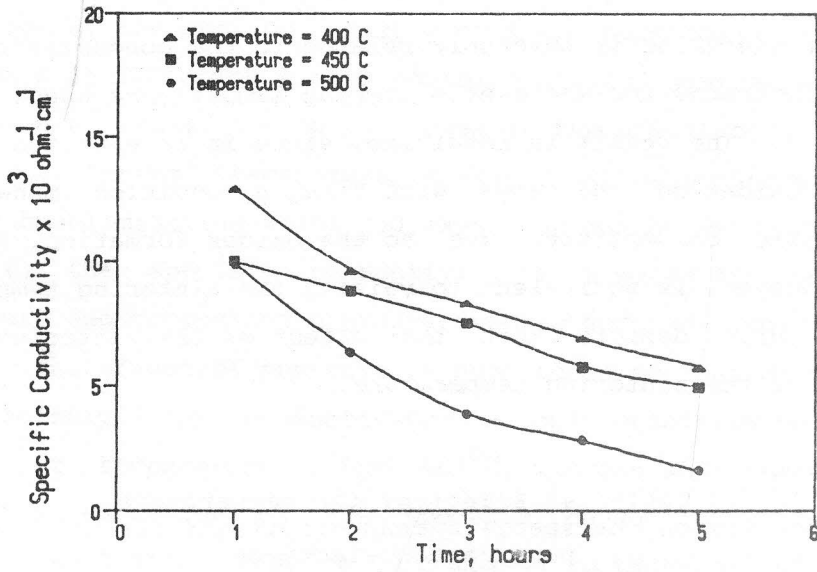
Figure 2: Effect of sintering time and temperature on the specific conductivity of the CRCE [C:Cu=3:1, P=1.04 ton/sq.cm, binder=1%]
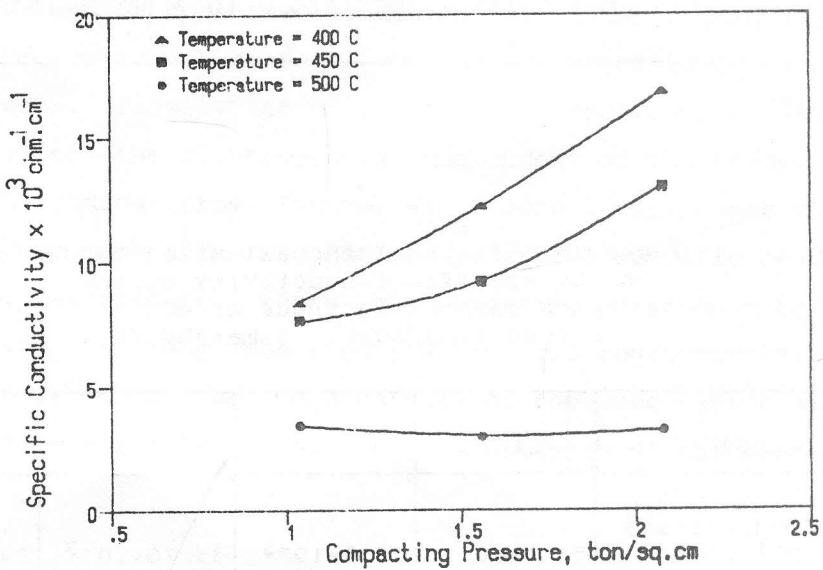

Figure 3: Effect of the compacting pressure and the sintering temperature on the specific conductivity of the CRCE [time=3hrs, C:Cu=3:1, binder=1%]

The time of sintering is inversely related to the conductivity of the composite electrodes for whatever sintering temperature used, as shown in Figure 2. The result is intuitive, since it is expected that the extent of oxidation increases with time, a condition amenable to a lower specific conductivity due to the oxides formation. Prolonged heating, however, is equivalent to raising the sintering temperature. The Figure also depicts that the effect of the sintering time is independent of the sintering temperature.

Table (4) Effect of the temperature
on the specific conductivity of the
pure carbon electrode
P=1.04 ton/sq.cm, time=3hours , binder=1%

Temp. (°C)	400	450	500
Conductivity $\Omega^{-1}.cm^{-1}$	$33.7*10^{-3}$	$35.0*10^{-3}$	$31.6*10^{-3}$

Table (5) Effect of the extent of binder
on the specific conductivity of the
pure carbon electrode at 400°C
P=1.04 tons/sq.cm, time=3hours

Binder %	0.0	0.5	1.0	1.5
Conductivity $\Omega^{-1}.cm^{-1}$	$58.1*10^{-3}$	$33.3*10^{-3}$	$33.70*10^{-3}$	$24.3*10^{-3}$

The effect of the applied pressure on the conductivity is illustrated in Figure 3 at different sintering temperatures. Generally, increasing the pressure leads to an increase in the specific conductivity at constant sintering temperature. Pressure serves to increase areas of contact by eliminating voids and expelling air or entrapped gases. As a result, the specific conductivity is expected to rise. Sintering temperature and compacting pressure seem to work adversely; at $500^\circ C$ however, the effect of pressure is overridden by that of temperature. More precisely, the conductivity is only sensitive to the applied pressure at temperature below $500^\circ C$, whereas at a temperature of $500^\circ C$ the variation of the specific conductivity is minimal $(2.4*10^{-3}$ to $3.2*10^{-3}$ ohm^{-1}cm^{-1}) compared to those at 400 and $450^\circ C$.

The presence of the binder slightly affects the specific conductivity of the CRCE. The stearic acid oxidizes and volatilizes at the used temperatures, and is consequently driven off. This in turn may lead to micro-void formation, therefore lowering the specific conductivity of the electrodes. Finally the effect of the carbon/copper ratio on the conductivity of the electrodes is independent of the binder content, as one can deduce from Figure 4. Figure 5 shows that the binder content is not much affecting the change of the specific conductivity at a high temperature, where the oxidation phenomenon is of prime responsibility for the observed low specific conductivity. Table 5, however, shows that the conductivity of the pure carbon electrodes depends, but to a limited extent, on the presence of the binder.
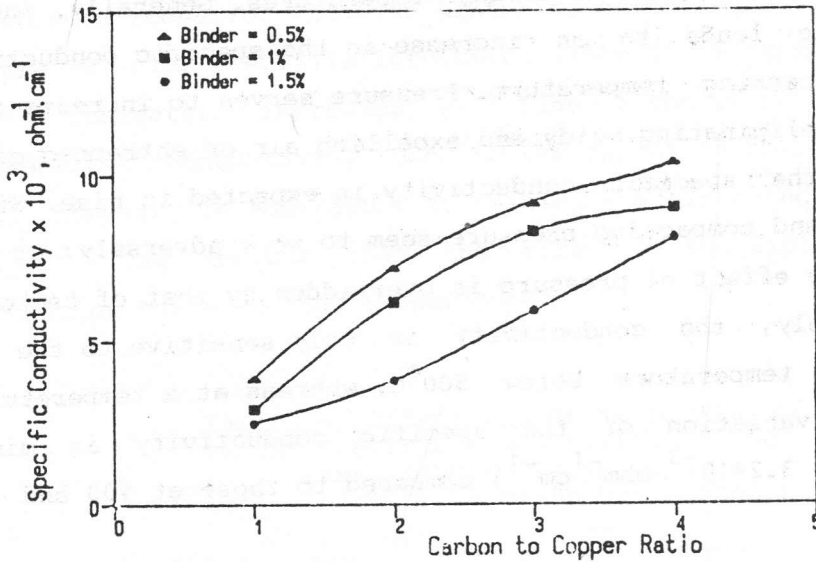
Figure 4: Effect of the carbon to copper ratio and the binder content on the specific conductivity of the CRCE [time=3hrs, P=1.04 ton/sq.cm, T=400°C]
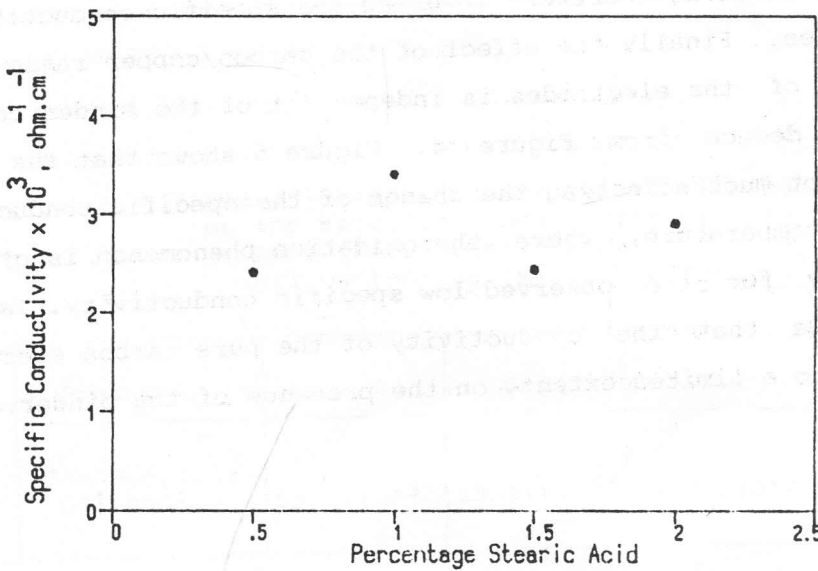

Figure 5: Effect of the binder content on the specific conductivity of the CRCE at 500°C [C:Cu=3:1, P=1.04 ton/sq.cm, time=3hrs]

It should be recorded, however, that this work has been undertaken under oxidizing sintering conditions, which, in turn, limited the variations of the processing variables investigated. Furthermore, the effect of the stearic acid in reducing oxidation of surfaces has been, obviously, hindered. An integrated experimental work would rather be conducted under a reducing atmosphere in order to better improve the specific conductivity of the CRCE.

4. Conclusions

From the foregoing analysis the following may be concluded:
1. Sintering temperatures are limited by an upper bound of $500^\circ C$.
2. The specific conductivity of the CRCE is reversely related to each of time, temperature of sintering and binder content.
3. The specific conductivity of the CRCE is proportionally related to the ratio of carbon to copper and the compacting pressure.
4. The presence of the binder slightly affects the specific conductivity of the CRCE.
5. The copper phase is more influencing the response of the CRCE than does the carbon phase.
6. Severe limitations are imposed on the response of the CRCE due to the utilized oxidizing sintering atmosphere.

Acknowledgment

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