

# FLEXIBLE-GRAPHITE-BASED POROUS COMPOSITE ELECTROCHEMICAL ELECTRODE EXHIBITING HIGH ELECTRICAL CONDUCTIVITY

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## Introduction

Electrodes are needed for batteries, fuel cells, supercapacitors, electrochemical sensors and other electrochemical devices. An electrode involving an electrochemically active species that is poor in electrical conductivity requires the presence of an electrically conductive species in the electrode for rendering conductivity to the electrode. Manganese dioxide ( $\text{MnO}_2$ ) [1] and lithium cobalt oxide ( $\text{LiCoO}_2$ ) [2] are examples of such electrochemically active species.

Electrically conductive species used in such an electrode is commonly in the form of discontinuous carbon fillers, such as carbon black [1,2], graphite particles [3-5] and carbon nanofiber [1,2,6]. The filler is commonly mixed with the electrochemically active particles in the presence of a binder, which is typically nonconductive. Examples of binders are PTFE and PVDF. The binder is commonly introduced in the form of particles. Upon heating, the binder flows and provides the binding ability. The binder serves to bind the ingredients together to form a bulk form, such as a sheet.

Instead of using a binder to join the conductive species to the electrochemical species in the electrode, it is possible to deposit the electrochemical species on a conductive substrate, such as carbon black. Although the absence of a binder is attractive from the electrical conduction point of view, the deposition methods are more expensive, more complicated and less versatile (in terms of the choice of electrochemical species) than methods involving a binder.

A problem with the abovementioned electrode technologies that involve binders relates to the high electrical resistivity, which stems from (i) the contact resistance at the interface between adjacent units of the conductive filler, and (ii) the high contact resistance at the interface between the conductive substrate and the electrochemically active species due to the intervening binder. The resistivity of a  $\text{MnO}_2$  electrode with discontinuous graphitized carbon nanofiber as the conductive additive is  $1.0 \Omega\cdot\text{cm}$  [1]; the resistivity of an  $\text{LiCoO}_2$  electrode with discontinuous carbon nanofiber as the conductive additive is  $1.4 \Omega\cdot\text{cm}$  [6]. Another problem relates to the detrimental effect of the binder on the electrolyte permeability of the electrode, and the consequent reduced degree of utilization of the electrochemically active component. Yet another problem relates to the limited chemical resistance of the binder.

This paper alleviates the problems mentioned above by eliminating the need for a binder, while maintaining low cost, process simplicity and versatility. This is achieved by exploiting the mechanical binding that is inherent in the formation of flexible graphite from exfoliated graphite. This paper uses no conductive filler, but it uses a graphite matrix. The graphite is in the form of flexible graphite. The electrochemically active component is present as a particulate filler in the flexible-graphite-based composite. Due to the porosity of flexible graphite, the electrolyte permeability is high. Due to the flexibility of flexible graphite, the electrode is flexible, in contrast to the brittleness of the ceramic-based electrodes of the prior art. Due to the strong electrical connectivity in the flexible graphite, the electrical resistivity is low. Furthermore, flexible graphite is attractive for its chemical resistance, thermal stability, thermal conductivity, low thermal expansion coefficient, low density, shapability (through cutting or molding) and low manufacturing cost. Although this study uses  $\text{MnO}_2$  as the electroactive component, the technology described here may be applied to particles other than manganese dioxide.

## Experimental methods

The manganese dioxide powder contains 82-85%  $\text{MnO}_2$ . The as-received particles of particle size of 50-70  $\mu\text{m}$  are reduced in average size to 4  $\mu\text{m}$  by ball milling.

The exfoliated graphite was obtained by rapid furnace heating of acid-intercalated natural graphite flake of typical mean size 0.25 mm. The worms are of length 2-4 mm.

Composites are prepared by compression of a mixture of exfoliated graphite and  $\text{MnO}_2$  particles, the weights of which are controlled, such that the resulting composite contains 53 wt.%  $\text{MnO}_2$ . The mixing is conducted for 24 h using a ball mill without grinding medium. The compression of the mixture is conducted in a cylindrical mold of length 45 cm and inner diameter 31.75 mm by applying a uniaxial pressure of 11.2 MPa via a matching piston. Each resulting specimen is a disc of diameter 31.75 mm and thickness around 0.5 mm.

Each disc obtained by compression is cut by using a knife into a number of specimens, which are used for electrical resistivity measurement in the in-plane direction (2 specimens per disc), electrical resistivity measurement in the out-of-plane direction (2 specimens per disc) and for water absorptivity measurement (2 specimens per disc). Each specimen obtained by cutting has all of its edges lightly sanded in order to remove the sheared carbon layers that may be present.

The electrical resistivity is measured by using the four-probe method, with silver paint in conjunction with copper wire serving as electrical contacts.

The absorptivity test is conducted by immersing each specimen in deionized water for controlled amounts of time (1-36 h) and determining the water uptake by weighing.

## Results and discussion

The composite contains 15 vol.%  $\text{MnO}_2$ , 29 vol.% solid graphite (nonporous) and 56 vol.% air. The air volume fraction is much higher than that expected if the composite

consisted of two phases, i.e.,  $\text{MnO}_2$  and similarly prepared flexible graphite (without  $\text{MnO}_2$ ). Without  $\text{MnO}_2$ , the material contains 60 vol.% solid graphite and 40% air. Thus, the porosity is increased by the addition of  $\text{MnO}_2$ .

Both the in-plane and out-of-plane resistivity values are increased by the presence of  $\text{MnO}_2$ . The in-plane resistivity is increased by 10%, while the out-of-plane resistivity is increased by 40%. The calculated resistivity for the composite, as obtained by the Rule of Mixtures (i.e., the conductivity of the composite is equal to the conductivity of flexible graphite multiplied by the volume fraction of flexible graphite, with the conductivity of  $\text{MnO}_2$  taken as zero), is higher than the corresponding measured value for both in-plane and out-of-plane directions. This means that the graphite maintains connectivity of its conduction path in the presence of  $\text{MnO}_2$  particles for both in-plane and out-of-plane directions. The  $\text{MnO}_2$  slightly disrupts the out-of-plane conduction, but does not disrupt the in-plane conduction.

The electrical anisotropy, as expressed as the ratio of the out-of-plane resistivity to the in-plane resistivity is increased slightly by the presence of  $\text{MnO}_2$ . The anisotropy is 24 without  $\text{MnO}_2$  and is 31 with  $\text{MnO}_2$ . This effect of  $\text{MnO}_2$  is consistent with the notion that  $\text{MnO}_2$  disrupts the out-of-plane conduction more than the in-plane conduction.

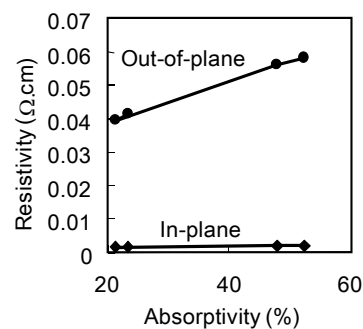
Both the in-plane and out-of-plane resistivity values of the flexible-graphite-based  $\text{MnO}_2$  composite are much lower than the resistivity of 1  $\Omega\cdot\text{cm}$  or above for the composite in the form of a mixture of  $\text{MnO}_2$  particles and carbon particles or fibers (including graphitized carbon nanofiber) held by a polymeric binder [1]. The low resistivity of the composite of this work is attributed to the high degree of electrical connectivity of the flexible graphite matrix of the composite. On the other hand, the  $\text{MnO}_2$  volume fraction is lower in this work than that in prior work [1].

The water absorptivity, as indicated by the fractional mass gain for a selected time of water immersion, is considerably increased by the presence of  $\text{MnO}_2$ . For a given specimen, the water absorption increase is most significant during the first 12 h of water immersion; afterward, the water absorption is incremental. The absorptivity at 12 h is increased by 125% by the presence of  $\text{MnO}_2$ .

A fractional mass gain of 24% for the unmodified flexible graphite corresponds to 31% filling of the pores by water. This value is obtained by a simple calculation based on the abovementioned density and porosity of the unmodified flexible graphite. This means that only 31% of the pores in the unmodified flexible graphite are accessible. A similar calculation for the composite, which exhibits water absorptivity up to 52-58%, shows that all of the pores are filled by water. In other words, the presence of  $\text{MnO}_2$  causes the fraction of pores that are accessible by water to increase from 31% to 100%. This finding is consistent with the abovementioned slight disruption of the out-of-plane conduction by the  $\text{MnO}_2$ .

Fig. 1 shows the correlation between the absorptivity at 12 h and the resistivity, with both quantities of each data point

measured on the same disc. A higher in-plane or out-of-plane resistivity correlates with a higher absorptivity.



**Fig. 1** Correlation of the resistivity and the absorptivity.

## Conclusions

A flexible porous  $\text{MnO}_2$  electrode of exceptionally low electrical resistivity (0.057  $\Omega\cdot\text{cm}$  in the out-of-plane direction and 0.0019  $\Omega\cdot\text{cm}$  in the in-plane direction) and high water (electrolyte) absorptivity is obtained using flexible graphite as the matrix and  $\text{MnO}_2$  particles as the filler. In contrast, the resistivity is 1  $\Omega\cdot\text{cm}$  or above for  $\text{MnO}_2$  electrodes made using the conventional method that involves a conductive additive and a binder [1,6]. The  $\text{MnO}_2$  causes the fraction of pores that are accessible by water to increase from 31% to 100%. The composite is obtained by compressing a mixture of exfoliated graphite and  $\text{MnO}_2$  particles in the absence of a binder. It contains 15 vol.%  $\text{MnO}_2$ , 30 vol.% solid graphite (nonporous) and 55 vol.% air. The  $\text{MnO}_2$  particles are of size 6-9  $\mu\text{m}$ . Relative to the unmodified flexible graphite, the composite exhibits higher resistivity (10% higher in-plane and 40% higher out-of-plane), 125% higher absorptivity and higher porosity. The  $\text{MnO}_2$  slightly disrupts the out-of-plane conduction, but does not disrupt the in-plane conduction. The resistivity and absorptivity are correlated.

## References

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