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Dielectric constant and electrical conductivity of carbon black as an electrically conductive additive in a manganese-dioxide electrochemical electrode, and their dependence on electrolyte permeation

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ABSTRACT

The relative dielectric constant and electrical conductivity of electrochemical electrodes with manganese-dioxide (MnO_2) particles mixed with carbon black (CB, the most common electrically conductive additive) are reported, with unprecedented determination of the decoupled CB properties and their dependence on the MnO_2 volume fraction. The electrolyte is 15 vol.% sulfuric acid. As the CB proportion increases, the CB electrical conduction connectivity increases, while the CB dielectric connectivity decreases (due to decreasing squishing by the MnO_2). The minimum MnO_2 content for squishing the CB to the extent of enhancing the CB polarizability is 65 vol.%. The electrolyte enhances the CB conduction/dielectric connectivity. Without electrolyte permeation, as the CB proportion increases from 14 to 30 vol.% (the MnO_2 proportion correspondingly decreasing from 69 to 59 vol.%), the CB resistivity decreases from 236 to 165 Ω cm and the CB relative dielectric constant decreases from 53 to 12 (leveling-off below 65 vol.% MnO_2), suggesting decreasing CB polarizability as CB is less squished. With complete electrolyte permeation, as the CB proportion increases from 18 to 25 vol.%, the CB resistivity decreases from 49 to 34 Ω cm and the CB relative dielectric constant decreases from 29 to 22. Without MnO_2, the CB conduction connectivity is the highest.

1. Introduction

Manganese dioxide (MnO_2) is a widely used active electrochemical electrode material that is used in the form of particles [1], with major applications including dry-cell batteries, such as the alkaline battery and the zinc–carbon battery [2,3]. In the alkaline battery, zinc is the anode while MnO_2 is the cathode; both the anode and the cathode are in the form of electrolyte-based particle pastes. In addition, MnO_2 is used as electrodes in supercapacitors in the form of pseudocapacitors [4–15]. In the pseudocapacitor, sulfuric acid is often used as the electrolyte to provide H^+ ions (protons), which react with the MnO_2 to cause the reduction of MnO_2 during charging; the opposite reaction (oxidation) occurs during discharging.

Due to its inadequate electrical conductivity, MnO_2 is commonly mixed with a conductive additive. The most common

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conductive additive used in practice is carbon black (CB) [16–20], although graphene, graphene oxide and carbon nanotubes are starting to be used [21–27].

The CB is attractive for its low cost, squishability and long history of effective use as a conductive additive. The squishability refers to its extensive compressibility, which results from the fact that carbon black is in the form of porous aggregates of nanoparticles. Due to the squishability, CB spreads upon being compressed between the MnO_2 particles, thereby promoting the electrical connectivity of the CB amidst the MnO_2 particles. In contrast, carbon nanofiber (CNF, originally known as carbon filament) is not squishable. Thus, in spite of its large aspect ratio, CNF (particularly if it is not graphitized) is not as effective as CB for enhancing the conductivity of an MnO_2 electrode [3,28], even though it is more effective than CB for providing a conductive carbon compact in the absence of MnO_2 particles [3]. The electrical resistivity of a dry compact of MnO_2 particles and CNF (16.6 vol.%) is down to 8 Ω cm, whereas that of a dry compact of MnO_2 particles and CB (15.2 vol.%) is down to 3 Ω cm [3]. In contrast, the resistivity of a dry compact of CNF (without MnO_2) is down to 0.020 Ω cm, whereas that of a dry compact of CB (without MnO_2) is down to 0.046 Ω cm [25]. The presence of the stiff MnO_2 particles facilitates the squishing of the CB located between the particles, thereby causing the CB to be highly effective (even more effective than CNF) for enhancing the conductivity. Without the MnO_2 particles, the squishing of the CB is less, so that the CB becomes less effective than CNF for providing low resistivity. The CB is also more effective than natural graphite and graphitized mesophase pitch for enhancing the conductivity of an MnO_2 electrode [28].

A high value of the relative dielectric constant (i.e., the real part of the relative permittivity) is desired for the electrolyte and the electrodes of a supercapacitor (double-layer capacitor). In contrast, for a battery, a low value of the relative dielectric constant is desired for the electrodes, as electric polarization in an electrode is disadvantageous to battery performance. Low values of the volume resistivity of the electrolyte and electrodes are desired for both supercapacitors and batteries in order to minimize the internal resistance of the electrochemical cell. In particular, a low volume resistivity of the electrode helps the transmission of the applied electric potential from the electrical contact to the electrode–electrolyte interface.

Prior work on electrodes of MnO_2 with carbon has emphasized testing in the electrochemical cell level, using techniques such as cyclic voltammetry, charge–discharge testing and electrochemical impedance spectroscopy [16–27,3], with little attention on testing in the material level [3,28]. The cell-level testing does not allow decoupling of the contributions by the cell components, such as the electrodes and the electrolyte. As a consequence, it is commonly assumed that MnO_2 is completely non-conductive, while the carbon is conductive, with negligible polarizability. For rigorous understanding of cell behavior and precise design of electrochemical cells, it is important to go beyond this assumption by determining the electrical conductivity and relative dielectric constant of each component of the electrode (MnO_2 and carbon). Both the dielectric behavior and the conduction behavior are important for understanding cell performance. The information is valuable for guiding electrode and cell design.

Although prior work has been directed at studying either the electrochemical cells with a combination of MnO_2 and carbon as an electrode [16–27,3] or the MnO_2–carbon electrode by itself, it provides information on the cell or electrode performance without decoupling the contributions of MnO_2 and carbon to the cell or electrode behavior. Due to the squishing of the CB in the presence of MnO_2 [3], the structure of the CB is expected to be affected by the presence of MnO_2. Without the decoupling, the structure and associated properties of the CB cannot be effectively studied. This work provides this decoupling for the first time.

Prior work has reported the electrical resistivity of dry (without an electrolyte) MnO_2–CB compacts [3,28] and the relative dielectric constant and electrical resistivity of dry CB compacts (without MnO_2) [29], and CB electrolyte-based pastes (without MnO_2) [29], with the electrolyte being 15 vol.% sulfuric acid. With the goal of studying the behavior of the CB in an MnO_2 electrode, this work addresses systematically dry MnO_2 compacts (without CB), dry MnO_2–CB compacts, MnO_2 electrolyte-based pastes (without CB) and MnO_2–CB electrolyte-based pastes.

This work is mainly directed at studying the resistivity and relative dielectric constant of the CB in an MnO_2 paste electrode with the liquid in the paste being the electrolyte and with various proportions of MnO_2 and CB in the paste. A fundamental scientific question addressed in this paper relates to the effects of the presence and volume fraction of the MnO_2 on the structure and properties of the CB in the electrode.

2. Experimental and analytical methods

The approach used for achieving the decoupling mentioned in Section 1 involves measuring the resistance and capacitance of (i) the dry MnO_2 and MnO_2–CB compacts (for determining the quantities pertaining to the MnO_2 and CB in the absence of an electrolyte), (ii) an electrolyte-containing paper towel (for determining the quantities pertaining to the electrolyte), and (iii) the MnO_2 and MnO_2–CB electrolyte-based pastes (for determining the quantities pertaining to the MnO_2 and CB in the presence of the electrolyte). The measurement of each property is conducted for three specimen thicknesses, thereby decoupling specimen volumetric and specimen-contact interfacial quantities (Fig. 1). The contact refers to the electrical contact to the electrode.

This approach was previously used to study carbon (without MnO_2) electrodes [29]. However, this approach has not been previously used to study MnO_2 electrodes, whether with or without carbon. The value of this approach relates to its ability to decouple the volumetric and interfacial quantities and to decouple the contributions from the various constituents in the electrode. Prior to Ref. 29, work on carbon, MnO_2 or other electrode materials measured the capacitance with the volumetric and interfacial contributions as a lumped quantity, without decoupling. In other words, the prior work assumed that the interfacial contribution is negligible.