

Battery in the Form of a Soil-Matrix Composite

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Abstract: This work has shown the feasibility of a soil-based battery, in which the electrolyte (soil) was continuous throughout the anode, cathode, and electrolyte. The soil contained 49 wt.% water. The battery was in the shape of a soil-based monolithic slab and involved an anode (zinc, particle size 7 μm , acetic acid washed), a cathode (MnO_2 , particle size 40 μm), and an electrically conductive additive (carbon black, particle size 30 nm). A battery was composed of three successive layers: a cathode layer (a soil-matrix MnO_2 particle composite, 12 wt.% MnO_2 , 15 mm thick), an electrolyte layer (soil, 2 mm thick), and an anode layer (a soil-matrix zinc particle composite, 9 wt.% Zn, 5 mm thick). After assembly, it was compacted at a pressure of 1.67 MPa. The soil electrolyte exhibited resistivity of $220 \Omega \cdot \text{cm}$ and a relative dielectric constant of 29 (1 kHz). The soil-based battery discharged at 10 mA (0.25 mA/cm^2) and exhibited open-circuit voltage up to 0.24 V, initial running voltage up to 0.17 V, power output up to $43 \mu\text{W/cm}^2$, capacity up to 179 mAh, and fraction of zinc consumed up to 0.06. The running voltage decreased continuously during discharge. The soil-based battery was much superior to a previously reported cement-based battery. **DOI:** 10.1061/(ASCE)EY.1943-7897.0000101. © 2014 American Society of Civil Engineers.

Author keywords: Battery; Soil; Zinc; Manganese dioxide; Electrical resistivity; Dielectric constant.

Introduction

Due to the rising cost of fuel and the environmental pollution (including global warming) resulting from the burning of fuel, there is urgent need for clean and renewable energy, such as that generated by fuel cells, batteries, solar cells, thermoelectric devices, and windmills. Among these sources of energy, batteries constitute the most developed source. However, their limited energy density makes conventional batteries (which are quite small) unable to provide large amounts of energy. For example, a battery-operated car would require the entire trunk of the car to be filled with batteries. As a result, batteries are only used as power sources for small devices, such as digital cameras, and the role of batteries in alleviating the energy crisis is small.

A battery consists of an anode (the electrode that is an electronic conductor and undergoes chemical oxidation during the discharge of the battery) and a cathode (the electrode that is an electronic conductor and undergoes chemical reduction during the discharge of the battery), which are separated by an electrolyte. During discharge, a voltage appears between the anode and the cathode.

Batteries and fuel cells suffer from (1) the safety (leakage) and environmental problems associated with the electrolyte in the usual case where the electrolyte is a liquid (Aurbach and Schechter 2004; Blomgren 2003; Nazri 2004; Webber and Blomgren 2002; Wilkes 2003), (2) the poor interface (Edstroem et al. 2004; Ross 2006)

between the electrodes (anode and cathode) and the electrolyte and the inadequate room-temperature ionic conductivity of the electrolyte in cases where the electrolyte is a solid (Notten et al. 2007; Sadoway 2004; Takada et al. 2004), and (3) the limited amount of energy that can be provided due to size and mass limitations.

One of the problems of conventional portable batteries relates to the electrolyte, which is an ionic conductor that serves as the medium between the anode and the cathode in a battery. There are two classes of electrolyte: liquid electrolytes and solid electrolytes. Due to the high mobility of ions in a liquid compared to that of ions in a solid, liquid electrolytes are better for battery performance. Furthermore, liquid electrolytes are much less expensive than solid electrolytes. In addition, the interface between the electrolyte and an electrode is more intimate when the electrolyte is a liquid rather than a solid. The intimacy of the interface causes the resistance associated with this interface to be relatively low. However, a serious shortcoming of liquid electrolytes is associated with the tendency of leakage of the liquid electrolyte from the battery (Kim et al. 2008) and the environmental pollution that results from this leakage. In addition, a battery containing a liquid electrolyte must be sealed through proper packaging, and the packaging adds to the cost of battery manufacture. Examples of liquid electrolytes are aqueous solutions with dissolved salts. Water is itself an electrolyte. Examples of solid electrolytes are polymers that have been doped so that they contain ions. Other examples of solid electrolytes are ceramics that have their ions arranged in such a way that substantial movement of the ions within the ceramic solid is geometrically possible. The ionic conductivity of a solid electrolyte increases with increasing temperature. Solid electrolytes tend to have inadequate ionic conductivity at room temperature.

Electrokinetics is a tool for removal and supply of matter into or out from porous materials. Electrokinetic transport processes are used in civil engineering for repair and maintenance purposes and in environmental engineering for contaminant removal. Primary examples include desalination of concrete and soil remediation. However, the concept behind this paper is not electrokinetics; rather, it pertains to a battery that uses soil as the electrolyte.

Soil is the most abundant material on earth. The use of soil located in the ground as the electrolyte of a battery, with electrodes (zinc as the anode and copper as the cathode) placed in the ground,

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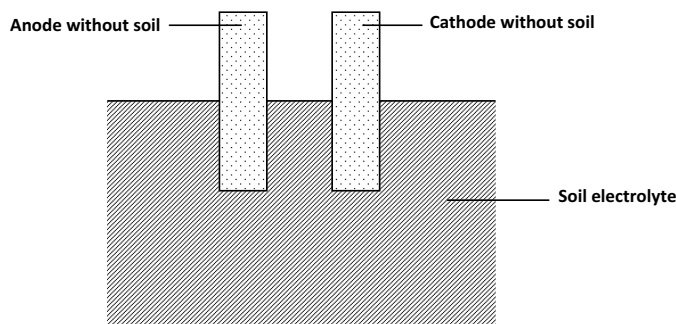


Fig. 1. Schematic illustration of the soil battery of prior art

has been previously reported (Gnomes'land 1998; Mahowald 2006). In the prior work, soil is not present in either anode (zinc) or cathode (copper), as illustrated in Fig. 1. The applications of the soil battery of the prior work are those that require low power, such as directing, watching, warning, lookout, camp lights, and sensors.

Gnomes'land (1998) uses two electrolytes such that the two electrolytes are separated by a partition. The electrolyte that surrounds the zinc anode is soil with zinc sulfate; the electrolyte that surrounds the copper cathode is soil with copper sulfate. Zinc sulfate serves to control the anodic character of the zinc, whereas copper sulfate serves to control the cathodic character of the copper. Moreover, zinc sulfate and copper sulfate provide ions that help the ionic conductivity of the electrolyte. However, they are soil contaminants that can result in acidic soil.

The soil battery of Gnomes'land (1998) and Mahowald (2006), as illustrated in Fig. 1, comprises (1) an anode (e.g., zinc metal), (2) a cathode (e.g., copper metal), and (3) electrolyte(s) in the form of soil. The electrodes are separated from one another by soil, which serves as the electrolyte. Mahowald stated that the distance between the two electrodes is typically around one to two feet. The battery of Gnomes'land (1998) or Mahowald (2006) is an assembly of components in the top region of the soil in the ground. It is not a monolithic device. As a consequence, it is poor in handleability.

Another shortcoming of the concept of Gnomes'land (1998) and Mahowald (2006) is that the battery involving soil as the electrolyte is limited to one that is at the ground where the soil resides. This limitation is clearly implied by the battery configuration depicted by Gnomes'land (1998) and Mahowald (2006). In this configuration, the anode and cathode are embedded in soil, to the extent that the top of each electrode is accessible from above the soil for the purpose of making electrical connection. The bottom of the soil is not depicted in any of the drawings of Mahowald (2006), indicating the unlimited and indefinite depth of soil in the ground. Due to the large depth of the soil, the battery of Mahowald (2006) is not a portable device. Indeed, Mahowald (2006) does not discuss a soil battery that is portable and does not discuss the possible advantages of an electrolyte in the form of soil in comparison with electrolytes of portable batteries in the prior art.

Continuity is needed for electrical conduction, which is a phenomenon that occurs inside any electrode during battery operation. Continuity along the length of the anode and along the length of the cathode is implied by the electrical connections depicted at the top of the anode and at the top of the cathode in the battery configuration depicted in the drawings of Gnomes'land (1998) and Mahowald (2006). Indeed, the use of the term "zinc metal" by Mahowald (2006) to describe the anode implies a continuous piece of zinc metal, which is depicted in any of the drawings of Mahowald (2006), and the use of the term "copper metal" to describe the cathode implies a continuous piece of copper metal, which is also depicted in any of the drawings of

Mahowald (2006). An example of a continuous form is a rod. An example of a discontinuous form is a collection of particles.

Yet another shortcoming of the concept of Gnomes'land (1998) and Mahowald (2006) relates to the electrodes being limited to those in a continuous form. This form limits the electrode materials to those that are available in a continuous form, such that this form is mechanically and electrically suitable for use as an electrode material. Electrodes must be able to conduct electricity by the movement of electrons. However, some electrode materials are not conductive, so their use in a continuous form is not suitable. Some electrode materials, such as ceramic electrode materials (e.g., manganese dioxide) are mechanically brittle, so their use in a continuous form leads to mechanical fragility in the electrode. Due to this limitation imposed by the requirement of the electrodes to be in a continuous form and the limited choice of cathode materials that are in a continuous form, Gnomes'land (1998) and Mahowald (2006) discuss the use of copper as the cathode. However, copper is not suitable as a cathode material due to its chemical reactivity, particularly in the presence of water that is in soil.

A macroscopic form, such as a rod of diameter 1 mm, is to be distinguished from a microscopic form, such as a microfiber of diameter 10 μm . A microfiber can be continuous, but its small cross-sectional size makes it insufficiently rigid, even if the microfiber (such as carbon fiber) is one that is high in mechanical strength and modulus. The insufficient rigidity makes a microfiber unsuitable for use on its own as an electrode. The battery of Gnomes'land (1998) and Mahowald (2006) is made by placing two electrodes in soil. This method of making and this configuration imply that the electrodes must be sufficiently rigid and thus must be macroscopic in size. However, brittle materials such as ceramics are more fragile when they are macroscopic in size than when they are microscopic in size. This is due to the higher probability for the presence of a microcrack when the size is larger. The presence of a microcrack, which propagates under stress, tends to cause low mechanical reliability. The requirement of both macroscopic size and physical continuity makes the choice of electrode materials even more limited than the case in which only physical continuity is required.

The continuous form of an electrode means that the electrode-electrolyte interface is localized to the surface of the continuous electrode. This localization means that the performance of the battery is highly sensitive to the degradation or loosening of this localized interface. This is another shortcoming of the concept of Gnomes'land (1998) and Mahowald (2006).

Still another shortcoming of the concept of Gnomes'land (1998) and Mahowald (2006) relates to the configuration in which each electrode has its length perpendicular to the surface of the soil, as shown by the drawings of Gnomes'land (1998) and Mahowald (2006). This configuration is not suitable for making batteries in the shape of a slab. Furthermore, the large typical distance of one to two feet between the electrodes in the configuration of Mahowald (2006) causes the electrical resistance to be high for the current through the electrolyte between the two electrodes. In addition, the configuration of Mahowald (2006) causes the area of the electrode-electrolyte interface to be limited by the depth of embedment of the electrodes. This limitation results in a low rate of battery discharge (i.e., a low current capability) and a high electrical resistance of this interface because the electrical resistance is inversely proportional to the area of the conduction path. Furthermore, the configuration makes the battery not compact, thus limiting the energy density of the battery.

Both Gnomes'land (1998) and Mahowald (2006) do not provide any performance data to support the feasibility of the concepts disclosed by them. Thus, their concepts have not been shown to be feasible.

This paper is aimed at overcoming the shortcomings of previously reported soil-based batteries. In addition, it is aimed at providing a feasibility demonstration.

Concept

This paper provides a battery in the form of a soil-matrix monolithic device that uses soil as the electrolyte. The device can be portable or fixed at a location. The location is not limited to the ground where soil resides.

The use of an inexpensive and abundant material such as soil for batteries enables the development of large batteries. Furthermore, by incorporating the soil battery as a part of the soil ground, the battery does not consume extra space (because the ground is present anyway) and potentially provides or stores large amounts of energy.

Soil batteries may be used to provide emergency power. In addition, they allow a structure to generate power so that it does not have to rely totally on power that is delivered from a distance. Delivered power tends to be interrupted in storms, thus causing blackouts. The ability to generate energy provides a new level of smartness to smart structures.

Soil is an ionic conductor (also an electronic insulator) that is in the form of a semisolid. The solid part of soil comprises minerals, whereas the liquid part of soil comprises water. Water usually constitutes a significant part of soil. The water is contained in the pores between the mineral particles in addition to residing within minerals that are in the form of hydrates. Soil serves as the electrolyte because the water, minerals (such as clay anions), and plant nutrients (such as magnesium cations) in the soil promote ionic conductivity. The use of soil as an electrolyte is attractive due to the environmental compatibility of soil. In addition, the fact that water is naturally contained in soil means that the soil does not need to be packaged in a container. Therefore, the use of soil as an electrolyte provides the advantages of a liquid electrolyte while avoiding the disadvantages of a liquid electrolyte. In addition, the use of soil as an electrolyte provides the advantages of a solid electrolyte while avoiding the disadvantages of a solid electrolyte.

In the soil-based battery of this paper, the anode, cathode, and electrolyte all involve soil as the continuous matrix. In contrast, the anode, cathode, and electrolyte of soil batteries of Gnomes'land (1998) and Mahowald (2006) and those of conventional batteries (such as a conventional alkaline battery) do not have a common matrix material, but they are distinct materials that are assembled together. In the soil batteries of Gnomes'land (1998) and Mahowald (2006), the anode is zinc metal, the cathode is copper metal, and the electrolyte is soil. In a conventional alkaline battery, the anode is zinc metal, the cathode is a manganese dioxide compact, and the electrolyte is a salt liquid solution. For the soil batteries of Mahowald (2006), the assembly is held together by the large amount of ground soil around and below the battery. For the soil batteries of Gnomes'land (1998), the assembly is held together by a container [labeled D in Fig. 4 of Gnomes'land (1998)]. For a conventional alkaline battery, the assembly is held together by a container (often known as a can), which must be sealed due to the liquid electrolyte. In contrast, the soil-based battery of this paper does not require a container or a large amount of soil. It is in the form of a soil-matrix monolith. Water is held inside the soil. The monolithic structure results in good mechanical integrity, good handleability, and intimate interfaces between the electrolyte and either electrode. The resistance of the battery is decreased and the capacity of the battery is increased by the large geometric area of the electrodes.

This paper is directed toward providing a battery in the form of a monolithic soil-based slab, with the anode component, electrolyte component, and cathode component in the form of layers that are essentially parallel and are essentially in the plane of the slab, such that (1) the electrolyte component consists mainly of soil, (2) each layer extends essentially throughout the area of the slab, (3) the anode component and the cathode component are completely separated by the electrolyte component, (4) essentially the complete surface of the electrolyte component layer that is proximate to the anode component layer is in contact with the proximate surface of the anode component layer, and (5) essentially the complete surface of the electrolyte component layer that is proximate to the cathode component layer is in contact with the proximate surface of the cathode component layer.

The soil-based battery of this paper is novel in that it comprises an anode component, an electrolyte component, and a cathode component, each of which involves soil as a continuous constituent (the matrix), such that (1) the soil constituent is continuous essentially throughout the system, (2) the soil constituent provides the electrolyte function, (3) the electrolyte component consists mainly of soil, (4) the anode component comprises soil and an active material, (5) the cathode component comprises soil and an active material, and (6) the anode component and the cathode component are completely separated by the electrolyte component. In this work, the active component in the anode component is dispersed in the anode component, and the active component in the cathode component is dispersed in the cathode component.

An electrode active component that is nonconductive (i.e., unable to conduct electricity by the movement of electrons) requires the use of a conductive additive for the purpose of rendering sufficient electronic conductivity to the electrode. An example of a conductive additive is carbon black, which is in the form of nanoparticles (particles in the nanometer size range, e.g., 30 nm) that form aggregates (Lin and Chung 2007). Due to this morphology, carbon black is squishable (highly compressible). Due to the small size of the particles, carbon black is effective for filling small spaces (Lin and Chung 2007), such as the space between adjacent electrode active particles. An example of an electrode active component that is nonconductive is manganese dioxide. When an electrode active component is conductive (e.g., zinc), the use of a conductive additive may not be necessary. Nevertheless, the use of a conductive additive in this case still helps the electrical connectivity between adjacent conductive active particles. The proportion of conductive additive in an electrode needs to be sufficient to help the electrical connectivity in the electrode, but it should not be so high that the volume fraction of active component in the electrode becomes low.

Due to the moisture, oxygen, or other ingredients in the environment, a material may react with one or more such ingredients and thus become covered by a thin layer of a reaction product. When the material is conductive particles and the reaction product is nonconductive, the presence of the coating is detrimental to the electrical connectivity of the particles. For example, the material is zinc, which is conductive, and the reaction product is zinc oxide, which is nonconductive. In this situation, removal of the coating is needed to attain electrical connectivity among the particles. In the case of zinc particles, removal of the coating may be achieved by washing the particles with acetic acid. Following this washing, the particle should be rinsed to remove the residual acetic acid. Rinsing may be carried out with a liquid (e.g., ethanol) that evaporates after the rinsing.

The soil-based anode, soil electrolyte, and soil-based cathode may be integrated by layer-by-layer assembly. For example, the soil-based cathode layer is laid down first, followed by the electrolyte layer and then the soil-based anode layer, as illustrated in Fig. 2.

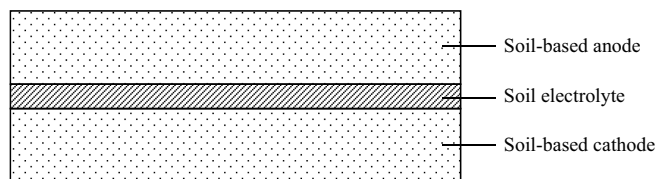


Fig. 2. Schematic illustration of a battery of this invention, with soil as the continuous constituent (matrix) in the cathode, electrolyte, and anode

Whether the anode or the cathode is at the bottom of the battery does not affect battery operation. However, to enhance mechanical stability, it is preferred that the electrode that is higher in density be at the bottom.

Due to the high porosity of natural soil and the detrimental effect of porosity on electronic conduction, consolidation of each layer (particularly the anode and cathode layers) during the layer-by-layer assembly and/or subsequent consolidation of the resulting three-layer monolith are recommended. The consolidation may be achieved by the application of pressure in the direction perpendicular to the layers. However, excessive consolidation is to be avoided because it tends to cause water to be squeezed out of the soil.

Although the electrolyte is an ionic conductor, the conductivity is limited. In a battery, the electrolyte layer is preferably thin. The thinner the electrolyte layer, the lower is the resistance.

The ionic conductivity of soil may be increased by the addition of a fertilizer or a related substance, which imparts additional ions to the soil. Thus, the soil in a battery of this invention may be soil that has been modified by the addition of one or more constituents that enhance the ionic conductivity. Fertilizers are attractive because they are environmentally friendly.

The thickness of the anode or cathode layer is governed by the amount of active material in the electrode. The greater the amount of active material, the longer is the battery discharge life at a given discharge current, i.e., the higher is the capacity of the battery. The ratio of the amount of active material in the anode layer to that in the cathode layer is governed by the electrochemical reaction, which usually consumes the anode and cathode active components to different extents.

Multiple soil batteries may be similarly formed in the same general location. For example, a soil battery may be formed on top of another one. A soil battery stack may thus be formed by electrically connecting components in series.

As for conventional batteries, a soil-based battery may be re-chargable if the electrochemical reactions are appropriately chosen. The charging is valuable for energy storage and for restoring the electricity-providing ability of a battery that has been discharged to a certain extent (whether by self-discharge or by intentional discharge). The charging ability is particularly important for large batteries that are associated with the ground.

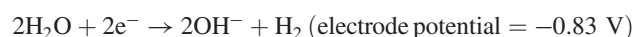
A battery involving zinc and manganese dioxide as active ingredients is not sufficiently rechargable. This is a disadvantage of the battery described earlier. Furthermore, for soil-based batteries that are parts of the ground, it is desirable for the batteries to contain only ingredients that are environmentally friendly. Active materials like zinc are not desirable. This is another disadvantage of the battery involving zinc and manganese dioxide as active ingredients.

An electrochemical cell works because of chemical dissimilarity between the anode and cathode regions of the cell. There are various ways to achieve dissimilarity. A cell can achieve the dissimilarity by involving different compositions for the anode and the cathode. A different method for a cell to achieve dissimilarity

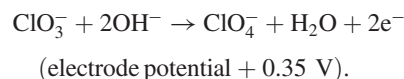
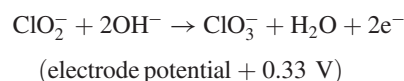
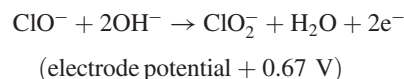
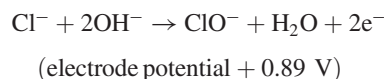
involves different compositions of electrolyte in the anode and cathode regions of the cell.

A form of soil-based battery that is environmentally friendly involves different compositions of soil in the anode and cathode regions of the battery. Modification of soil may be achieved by the use of environmentally friendly additives such as inorganic fertilizers. A fertilizer or a related chemical may be used to provide the active components for driving the electrochemical reaction. An example of electrochemical reactions that are environmentally friendly is provided as follows.

Either sodium chloride or calcium chloride is introduced to the soil in the anode region to provide Cl^- ions. During discharge, the cathodic reaction is



whereas the anodic reactions are (<http://en.wikipedia.org/wiki/Chlorine>)



The OH^- ions produced by the cathodic reaction drift through the electrolyte region to the anode region, where they are consumed by the anodic reaction. The water generated by the anodic reaction diffuses to the cathodic region, thus replenishing the water that is needed to drive the cathodic reaction during discharge.

The reversibility of the discharge reactions, as required for charging, requires that the hydrogen gas generated by the cathodic reaction during discharge remains in the cathodic region during the subsequent charging. This means that the battery needs to be sealed (as in carbon dioxide sequestration) if charging is desired.

The electrolyte region between the anode and cathode regions of the battery and the cathodic region can be simply the unmodified soil. The placement of a membrane in the electrolyte region between the two electrodes is recommended for the purpose of preventing the diffusion of NaCl or CaCl_2 from the anode region to the other cathode region. Active ingredients like zinc and manganese dioxide are not required. Current collectors in the form of electronic conductors (e.g., stainless steel mesh) should be placed in the anode and cathode regions for the purpose of directing electrons to flow between the anode and the cathode in the external electronic circuit. During discharge, electrons flow from the anode to the cathode. During charge, electrons flow from the cathode to the anode.

Experimental Methods

Materials

The soil used was garden soil from Scotts (Marysville, OH). The soil contained 32.96% SiO_2 , 7.66% Al_2O_3 , 7.69% CaO , 5.83% Fe_2O_3 , 2.45% MgO , 1.78% SO_3 , with 37.71% ignition loss.

Eight specimens of soil were dried at 110°C in a vacuum box (25 in. of mercury) 850 mbar for 1 h. Based on the weight before and after the drying process for each of these eight specimens, the proportion of water in the soil was found to be 0.49 ± 0.02 .

The zinc particle used as the active component in the anode was Zinc Dust 122 from Horsehead Corp. (Monaca, PA). It contained 99.3% zinc. The median particle size was 7 μm . The density was 7.452 g/cm³. Immediately prior to use, the surface of the zinc dust was cleansed of its native oxide by acetic acid washing followed by ethanol rinsing.

The manganese dioxide native powder (CAS No. 1313-13-9) used as the active component in the cathode was obtained from Fisher Scientific (Rochester, NY). The powder comprised the following principal components: MnO₂ 82–85%, quartz 1–3%, and barium compounds 1–2%. The average particle size was 40 μm . The density was 5.02 g/cm³.

The carbon black used as an electrically conductive additive in either electrode was Vulcan XC72R GP-3820 from Cabot Corp. (Billerica, MA). It was in the form of porous agglomerates of carbon particles of average size 30 nm.

The anode mix and the cathode mix were separately prepared by mixing the ingredients (Table 1) using a rotary mixer with a flat beater. The electrolyte preparation did not involve any mixing.

Characterization Methods

Each component was separately tested in terms of its electrical resistivity and relative dielectric constant, using specimens that were separately prepared for these tests. The relative dielectric constant related to the ability of ions to move in response to an applied electric field.

Electrical Resistivity Measurement

The electrical resistivity of the anode, cathode, and electrolyte was separately measured using specimens of length 62 mm in the direction of the resistance measurement and of cross-sectional dimensions 13 \times 12.5 mm. The two voltage contacts, which were symmetrically positioned with respect to the midpoint of the length and were placed in a perimeter around the specimen in planes perpendicular to the direction of resistance measurement, were 45 mm apart. The resistivity was given by the product of the resistance and the cross-sectional area divided by the distance between the two voltage contacts.

Resistivity measurement involved two methods that differed in the electrical contacts used for passing current during the measurement. In both methods, the voltage contacts were in the form of an electronic conductor (silver paint in conjunction with copper wires). In one method, the current contacts were electronic conductors, namely silver paint in conjunction with copper wires, such that they were 55 mm apart (symmetrically positioned with respect to the midpoint of the length), with each contact being placed in a perimeter around the specimen. In the other method, the current contacts were ionic conductors, namely an aqueous solution containing 0.33 mol/L of KOH and 0.13 mol/L NaOH and held by a sponge. A sponge was positioned at each end of a specimen of

length 62 mm. A copper foil was inserted in each sponge for the purpose of electrical connection to the current terminals of the multimeter.

An electronic conductor as the current contact does not allow ions to be injected into the specimen, whereas an ionic conductor as the current contact does not allow electrons to be injected into the specimen. Thus, the former tends to promote electronic conduction, whereas the latter tends to promote ionic conduction. However, the resistivity obtained by using the electronic form of current contacts is not simply the electronic conductivity, and that obtained by using the ionic form of current contacts is not simply the ionic conductivity. In a material that is high in conductivity due to the high concentration of a charge carrier, conduction by this carrier occurs significantly, whether the current contact is electronic or ionic. In this situation, the resistivity values obtained by the two methods are comparable.

In general, electrical resistivity measurement can be conducted by using either two electrical contacts (the two-probe method) or four electrical contacts (four-probe method). In the two-probe method, each of the two electrical contacts is for passing current as well as voltage measurement. In the four-probe method, the outer two contacts are for passing current, whereas the inner two contacts are for voltage measurement. In general, the four-probe method is more reliable, because the resistance of the voltage contacts is essentially excluded from the measured resistance between these contacts. In contrast, the contact resistance is included in the measured resistance in the two-probe method. When the specimen resistance is sufficiently high such that the contact resistance contribution is small, the two-probe method is reliable.

In this work, the two contacts used in the two-probe method were in the form of an electronic conductor (silver) and were positioned as for the inner contacts used in the four-probe method. The electrical resistance was measured by using a precision multimeter (Model 2001, Keithley, Cleveland, OH) operated in either the two-probe configuration or the four-probe configuration. The two-probe method was used to test three specimens of each type. To make sure that the results using the two-probe method were accurate, the four-probe method was used for testing a single specimen of each type.

Relative Dielectric Constant Measurement

The relative dielectric constant relates to the extent of ion movement in response to an applied electric field. Its value is preferably high for an electrolyte. This quantity was measured in this work by using disc-shaped specimens of diameter 12 mm and thickness 1.5 mm. Four specimens of each composition were tested. The value was calculated from the capacitance, which was measured by using the parallel-plate capacitor geometry and a precision impedance meter (Model 7600, Quadtech). The parallel plates (electrodes) sandwiching the specimen were copper discs of diameter 12 mm and height 2 mm. To avoid current flow between the plates, a thin Teflon (polytetrafluoroethylene) sheet of thickness 25 μm was placed between the specimen and each copper plate. A pressure of 3.5×10^5 Pa was applied to the stack in the direction perpendicular to the plane of the specimen in order to enhance the contact between the components in the stack. The capacitance was measured as C_s (with the specimen considered as an equivalent circuit consisting of a resistor and a capacitor in series) and C_p (with the specimen considered as an equivalent circuit consisting of a resistor and a capacitor in parallel). From the measured capacitance C (in F), the relative dielectric constant κ was calculated using the equation

$$\kappa = \frac{Cd}{\epsilon_0 A} \quad (1)$$

Table 1. Formulations of Soil-Based Anode, Electrolyte, and Cathode

Anode	Electrolyte	Cathode
Soil: 34 g	Soil: 40 g	Soil: 34 g
Zinc: 5 g (2.3 vol.%) ^a	—	MnO ₂ : 6.67 g (4.4 vol.%) ^a
Carbon black: 0.4 g	—	Carbon black: 0.67 g

^aCalculated from the weight and known density of the component and the volume of the specimen.

where $d = 1.55$ mm is the distance between the two electrodes; $A = 113.09$ mm² is the contact area; and $\epsilon_0 = 8.854 \times 10^{-12}$ F · m⁻¹ is the permittivity of free space. The frequencies used were 1 kHz and 1 MHz and the voltages used were 1.000 V and 100 mV.

Soil-Based Battery Preparation

The anode mix and the cathode mix were separately prepared by mixing, using a rotary mixer with a flat beater. After this, the cathode mix was put into a mold cavity and then compressed at a pressure of 1.67 MPa, using a matched piston and a hydraulic press. The electrolyte was then placed on the surface of the cathode mix in the mold. This was followed by compression again at 1.67 MPa. Finally, the anode mix was placed on the surface of the electrolyte. This was again followed by compression at 1.67 MPa. After this, the entire assembly was demolded and then stored in a sealed plastic bag.

The battery had dimensions 100 mm × 40 mm × 20 mm. The three layers in the battery were all in the plane of dimensions 100 mm × 40 mm.

Soil-Based Battery Testing

The open-circuit voltage of the battery was measured, followed by discharge testing. Both before the open-circuit voltage measurement and after the discharge testing, the DC electrical resistance measurement was performed in the direction perpendicular to the plane (layers) of the battery. From the measured resistance, the resistivity was calculated based on the measured dimensions. Fig. 3 is a photograph of a soil-based battery with two electrical leads protruding from each of the two electrodes.

The capacity of commercial alkaline batteries is typically characterized by constant-current discharge at 100 mA. However, a lower current (10 mA) was used to discharge the soil-based battery.

The electrical resistivity of a soil-based battery was measured in the direction perpendicular to the plane of the battery components by using the four-probe resistance measurement function of a precision multimeter (Model 2001, Keithley, Cleveland, OH).

Two electrical contacts in the form of silver paint in conjunction with copper wire were applied to each of the two opposite 100 × 40 mm surfaces of the battery. The two contacts on a surface were in the form of two hollow rectangular loops, both of which were centered with respect to the center of the specimen surface. Both loops were smaller than the specimen dimensions of 100 × 40 mm, such that one loop was smaller than the other and lay within the boundary of the other. The two loops on a surface did not contact one another. A battery was subjected to an open-circuit voltage measurement, with the inner loop contact on each of the two opposite surfaces used as leads connected to the multimeter.

Battery performance testing involved constant-current discharge at various controlled values of the current and measuring the running voltage versus discharge time until the voltage had dropped to zero. A pair of outer and inner contacts was embedded at the

middle plane (middle of the thickness) of the anode; another pair of outer and inner contacts was embedded at the middle plane of the cathode. Each contact was in the form of copper wire [0.020 in. (0.51 mm) diameter] coated with graphite colloid. The embedding was conducted during battery fabrication when the colloid was still wet.

During battery discharge, a constant current, as controlled by a DC current source (2400 Series, Keithley, Cleveland, OH), was passed from the cathode to the anode, using the outer one (90 × 35 mm² = 3,150 mm²) of the two rectangular loop contacts at each electrode. At the same time, the running voltage was measured across the two electrodes, using the inner one (70 × 25 mm² = 1,750 mm²) of the two loop contacts at each electrode.

The discharge current flowed from the cathode to the anode so that it was perpendicular to the large (100 × 40 mm) surfaces of the battery. The ability to make electrical contact to the large surface of an electrode rather than the small edge surface of the electrode was attractive for promoting uniform current density. In contrast, Gnomes'land (1998) and Mahowald (2006) disclosed the making of electrical contact to the small edge surface of each electrode, as shown by their drawings.

In the battery discharge testing, the DC current source was used to provide a constant current, which was 10 mA. During discharging, a negative test current was used, as described in the article "Battery Discharge/Charge Cycling Using Keithley Series 2400 SourceMeter Instruments" in the Keithley application note series. The running voltage of the battery was measured by using the multimeter. The positive end of the current source was connected to the cathode (the outer loop contact), while the negative end of the current source was connected to the anode (the outer loop contact). The positive end of the multimeter was connected to the cathode (the inner loop contact), while the negative end of multimeter was connected to the anode (the inner loop contact). During discharge, electrons travelled from the anode to the cathode through the current source. Thus, the voltage measured was positive. If the battery did not function while the current source supplied a DC current, the voltage detected by the multimeter would be negative.

Calculations based on the discharge results gave the fraction of zinc consumed by the end of discharge. The method of calculation is described as follows.

The amount of electrical charge (in C) that had gone through the electrical circuit is given by

$$Q = I \cdot t \quad (2)$$

where I = current (in A) provided by the current source; and t = entire time interval (in s) of a discharge test. The number of electrons involved is given by

$$n_e = Q/e \quad (3)$$

where e is the electronic charge = 1.6×10^{-19} C. Oxidation of one zinc atom releases two electrons; thus the number of reacted zinc atoms $n_{Zn} = n_e/2$.

Let the mass of zinc in the battery be M (in g). The number of zinc atoms contained in the battery is then given by

$$N_{Zn} = \frac{M \times N_a}{m_a} \quad (4)$$

where N_a = Avogadro number = 6.02×10^{23} ; and m_a = atomic mass of zinc = 65 g · mol⁻¹.



Fig. 3. Photograph of a soil-based battery

The fraction of zinc atoms oxidized is then given by

$$f = \frac{n_{Zn}}{N_{Zn}} = \frac{\frac{l \times t}{2e}}{\frac{M \times N_a}{m_a}} = \frac{l \times t}{M} \times \frac{m_a}{N_a \times 2e}$$

$$= \frac{l \times t}{M} \times \frac{65 \text{ g} \cdot \text{mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1} \times 2 \times 1.6 \times 10^{-19} \text{ C}}$$

$$= \frac{l \times t}{M} \times 3.37 \times 10^{-4} \text{ g} \cdot \text{C}^{-1} \quad (5)$$

Results and Discussion

Soil-Based Battery Component Formulation

The formulation of the soil-based anode and cathode is addressed in this section. The electrolyte was just the soil. The formulation was directed at providing the active ingredients in addition to rendering adequate electrical conductivity.

The formulations of the anode, cathode, and electrolyte are shown in Table 1. The proportion of carbon black was higher for the cathode than the anode due to the nonconductive nature of manganese dioxide, in contrast to the conductive nature of zinc.

The green (prior to compaction) anode, cathode, and electrolyte, as obtained by mixing, if applicable, were separately placed in high-density polyethylene mold cavities ($62 \times 13 \times 12.5$ mm for each cavity) and then compressed at a pressure of 1.67 MPa, using a matched piston (also made of high-density polyethylene) and a hydraulic press. The mold consisted of three side-by-side mold cavities, which were used for preparing three specimens at a time. These specimens were for measurement of the electrical resistivity along the length of each specimen.

Electrical Resistivity Results

The resistivity results are shown in Table 2. The resistivity values obtained by the four-probe and two-probe methods are quite close, indicating the validity of the two-probe method. For the same material (whether anode, cathode, or electrolyte), the resistivity values obtained by using electronic and ionic forms of current contacts are close, though the value is lower when the contacts are ionic. This can be explained by considering the high water content and the consequent high concentration of ions available for conduction. However, the similarity of the values obtained using electronic and ionic forms of current contact indicates that both ionic conduction and electronic conduction occur in the anode, cathode, and electrolyte. The presence of electronic conductivity in the electrolyte is not desirable because it will promote self-discharge of the resulting battery.

The anode exhibits the highest resistivity. The cathode and electrolyte exhibit similarly low values of resistivity. The relatively high resistivity of the anode is attributed to the high zinc volume fraction in the anode. Zinc is in the form of particles that are not adequately connected electrically, in spite of the carbon black

present. Therefore, the contribution of zinc to the conduction is low compared to that of water. Thus, the resistivity of the anode is higher than that of soil itself (the electrolyte), in spite of the carbon black present in the anode. The similarity of the resistivity of the cathode and electrolyte is due to the combination of manganese dioxide (which increases the resistivity) and carbon black (which decreases the resistivity) in the cathode.

Relative Dielectric Constant Results

Table 3 shows the relative dielectric constant for series and parallel configurations. The corresponding results for the series and parallel configurations were close. For any of the specimen types, the relative dielectric constant decreased with increasing frequency, as expected. At the same frequency, the relative dielectric constant was higher for the electrolyte than the anode or cathode and the values were similar for the anode and cathode. The high value for the electrolyte supports the effectiveness of the electrolyte.

Soil-Based Battery Formulation

Table 4 provides the battery formulation used in this work. Within a component of the battery, the composition is the same as that of the corresponding component shown in Table 1. The thickness of the cathode was typically twice that of the anode to satisfy the chemical reaction of the Zn-MnO₂ battery. The electrolyte layer was much thinner than either anode or cathode layer.

Soil-Based Battery Performance

Fig. 4 shows the constant-current (10 mA) discharge curves of soil-based battery 1. The running voltage started decreasing at the start of discharge and continued to decrease until the end of the discharge life. The resistivity at the end of the discharge is higher than the values in Table 2, probably because of the products of the discharge reaction. The resistivity before the discharge could not be measured because of the presence of the running voltage.

Table 5 summarizes the performance characteristics of soil-based batteries 1 to 6, which were identical in composition and

Table 3. Relative Dielectric Constant of Soil-Based Anode, Cathode, and Electrolyte, Each Obtained for the Series and Parallel Configuration of the Resistor and Capacitor in the Equivalent Circuit

Component	100 mV		1 V	
	1 kHz	1 MHz	1 kHz	1 MHz
Relative dielectric constant κ (series configuration)				
Anode	20 ($\pm 40\%$)	13 ($\pm 10\%$)	23 ($\pm 18\%$)	14 ($\pm 12\%$)
Cathode	28 ($\pm 17\%$)	15 ($\pm 12\%$)	24 ($\pm 24\%$)	14.2 ($\pm 6\%$)
Electrolyte	34 ($\pm 9\%$)	26 ($\pm 10\%$)	28 ($\pm 15\%$)	19 ($\pm 21\%$)
Relative dielectric constant κ (parallel configuration)				
Anode	21 ($\pm 15\%$)	13 ($\pm 9\%$)	22 ($\pm 16\%$)	13 ($\pm 13\%$)
Cathode	21 ($\pm 27\%$)	15 ($\pm 12\%$)	24 ($\pm 24\%$)	14 ($\pm 12\%$)
Electrolyte	30 ($\pm 27\%$)	25 ($\pm 10\%$)	29 ($\pm 15\%$)	18 ($\pm 19\%$)

Table 2. Measured Electrical Resistivity ($\Omega \cdot \text{cm}$) of Soil-Based Anode, Cathode, and Electrolyte

Measurement method	Anode	Cathode	Electrolyte
Electronic (two-probe) ^a	340 ($\pm 20\%$)	270 ($\pm 13\%$)	280 ($\pm 4\%$)
Electronic (four-probe) ^b	336.3	260.3	249.6
Ionic (four-probe) ^b	320 ($\pm 15\%$)	230 ($\pm 22\%$)	220 ($\pm 10\%$)

^aThree specimen tested.

^bOne specimens tested.

Table 4. Soil-Based Battery (22 mm Thick) Formulation

Anode (5 mm thick)	Electrolyte (2 mm thick)	Cathode (15 mm thick)
Soil: 34.2 g (90%)	Soil: 10.2 g	Soil: 65.45 g (85%)
Zinc: 3.42 g (9%)	—	MnO ₂ : 9.24 g (12%)
Carbon black: 0.384 g (1%)	—	Carbon black: 2.31 g (3%)

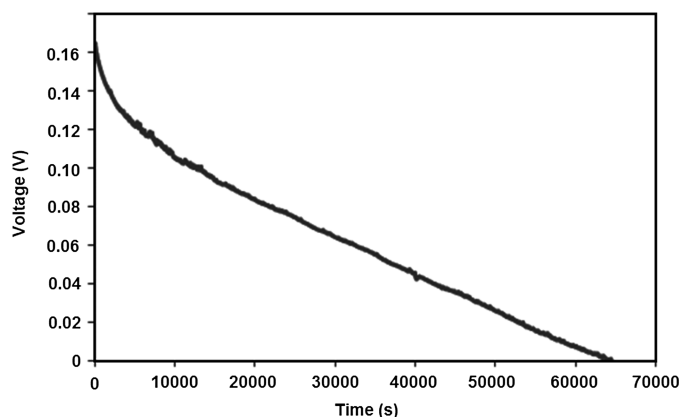


Fig. 4. Constant-current discharge of soil-based battery 1

Table 5. Performance of Soil-Based Batteries under Discharge at Current of 10 mA and Current Density of 0.25 mA/cm²

Battery number	1	2	3	4	5	6
Open-circuit voltage (V)	0.240	0.220	0.180	0.180	0.225	0.225
Initial running voltage (V)	0.170	0.160	0.120	0.120	0.160	0.160
Initial power output per unit area ($\mu\text{W}/\text{cm}^2$)	43	40	30	30	40	40
Discharge life (h)	17.9	11.4	7.2	10.7	12.5	11.1
Capacity (mAh)	179	114	72	107	125	111
Fraction of zinc consumed	0.06	0.04	0.03	0.04	0.04	0.04
Resistivity after discharge ($\Omega \cdot \text{cm}$)	1,400	1,200	1,200	4,200	1,400	1,400

preparation method. A higher initial running voltage tends to be associated with a longer discharge life. Among the six batteries, the highest fraction of zinc consumed was 0.06, as exhibited by battery 1. The highest capacity of 179 mAh was also exhibited by battery 1. The low zinc consumption is attributed to the inadequate electrical connectivity of the zinc particles in the anode. However, it may also be due to the reactivity of zinc with water in the soil and the electrical insulation nature of the reaction product. The difference in performance among batteries 1 to 6 indicates that control of the battery quality is inadequate.

Comparison of Soil-Based and Cement-Based Batteries

Recent work by two of the authors (Meng and Chung 2010) has shown the feasibility of a cement-based battery with set cement as the electrolyte, zinc as the anode, and manganese dioxide as the cathode and with the electrolyte being continuous throughout the anode, cathode, and electrolyte. Soil is a better electrolyte than cement, so a soil-based battery gives better performance than a cement-based battery.

The soil-based electrodes and electrolyte exhibited lower values of electrical resistivity and higher values of relative dielectric constant than the corresponding cement-based components. For example, the soil electrolyte had a resistivity of 220 $\Omega \cdot \text{cm}$ (as measured by using ionic electrical contacts), compared to the corresponding value of 910 $\Omega \cdot \text{cm}$ for the cement-based electrolyte. For the cement electrolyte, the resistivity measured by using ionic contacts is lower than that measured by using electronic contacts, whereas the resistivity measured by using electronic contacts is higher than that measured by using ionic contacts, indicating the

dominance of ionic conduction over electronic conduction in the electrolyte. For the soil electrolyte, the resistivities measured by using the two types of contacts are comparable, due to the very high ionic conductivity.

Soil-based batteries were superior to cement-based batteries in performance because of the higher ionic conductivity and higher relative dielectric constant of soil. The soil-based battery exhibited longer battery life, greater capacity, and higher consumption of active components. The soil-based battery was able to be discharged under a constant current up to 10 mA (current density = 125 $\mu\text{A}/\text{cm}^2$), providing power output up to 24 $\mu\text{W}/\text{cm}^2$, whereas the cement-based battery could only attain 120 μA (current density = 3.8 $\mu\text{A}/\text{cm}^2$), providing power output up to 1.4 $\mu\text{W}/\text{cm}^2$. Although the open-circuit and running voltages of the soil-based battery were lower than those of the cement-based battery (with 28 days of curing), the former had a greater capacity (23 mAh) than the latter (0.3 mAh) at similar weights and volumes.

Both soil-based and cement-based batteries were less effective than the commercial alkaline battery, probably because of the poor electrical connectivity of zinc (manganese dioxide) particles in the anode (cathode).

Conclusion

This work has shown for the first time the feasibility of a soil-based battery. The soil-based batteries are in the shape of a monolithic slab. This shape may be used for portable batteries and for batteries that are fixed at particular locations.

The soil-based batteries of this work involved active materials (zinc and MnO_2) and an electrically conductive additive (carbon black). A battery was composed of three layers: cathode, electrolyte, and anode. The thickness of the cathode was typically twice that of the anode to satisfy the chemical reaction of the Zn- MnO_2 battery. The three layers were prepared separately by mixing. To make a soil-based battery, a pressure of 1.67 MPa was applied to compact the slab.

The soil electrolyte exhibited resistivity of 220 $\Omega \cdot \text{cm}$, as measured by using current contacts in the form of an ionic conductor. The resistivity measured by using ionic contacts was lower than that measured by using electronic contacts, supporting the dominance of ionic conduction in the soil electrolyte. However, the resistivities measured by using the two types of contacts were comparable, due to the presence of both ionic and electronic conductivity. The soil electrolyte exhibited a relative dielectric constant of 29 (1 kHz).

The soil-based battery discharged at 10 mA (0.25 mA/cm²) and exhibited open-circuit voltage up to 0.24 V, initial running voltage up to 0.17 V, power output up to 43 $\mu\text{W}/\text{cm}^2$, capacity up to 179 mAh, and fraction of zinc consumed up to 0.06. The running voltage decreased continuously during discharge. The low performance compared to a commercial alkaline battery is probably a result of the inadequate electrical connectivity of zinc (manganese dioxide) particles in the anode (cathode).

Soil-based batteries were superior to cement-based batteries (Meng and Chung 2010) in performance because of the higher ionic conductivity and higher relative dielectric constant of soil. Soil is a better electrolyte than cement.

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