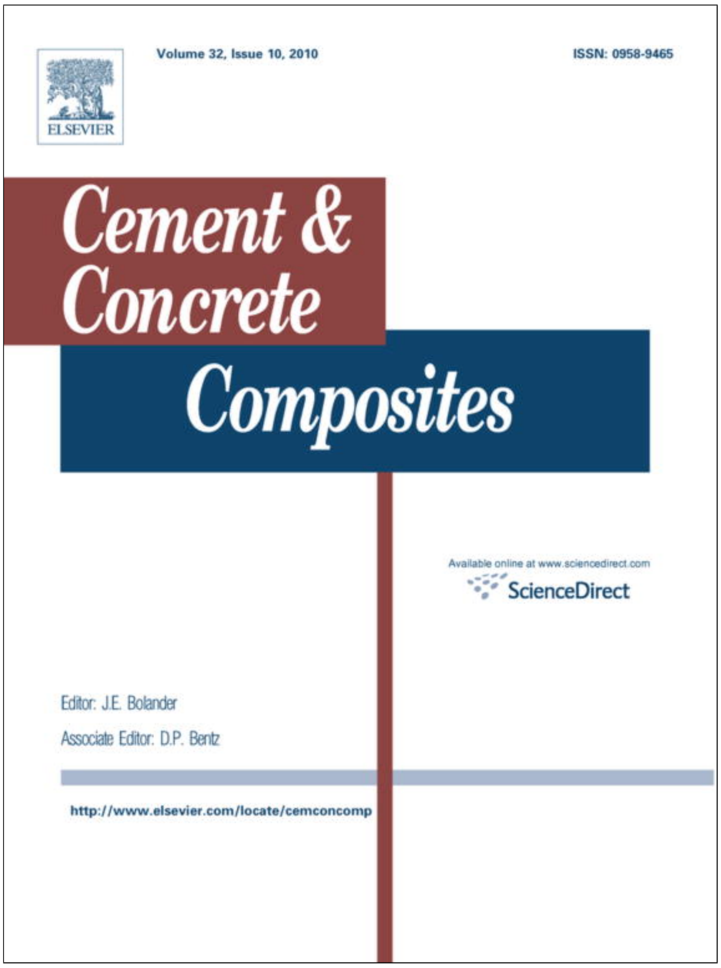

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Battery in the form of a cement-matrix composite

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ABSTRACT

Reported here is a battery in the form of a cement-matrix composite, with cement paste as the matrix, the pore solution in cement as the electrolyte, zinc particles dispersed in the matrix as the anode, manganese dioxide particles dispersed in the matrix as the cathode, and carbon black dispersed in the matrix as the conductive additive in both anode and cathode regions. The electrolyte is continuous throughout the battery, which consists of successively cast and co-cured anode, electrolyte and cathode layers. The anode layer (4 mm thick) comprises cement and zinc particles. The cathode layer (8 mm thick) comprises cement and manganese dioxide particles. The electrolyte layer (2 mm thick) is cement with an embedded piece of tissue paper for drying shrinkage control. The battery attained open-circuit voltage up to 0.72 V, current up to 120 μA (current density up to 3.8 μA/cm^2), power output up to 1.4 μW/cm^2, capacity up to 0.2 mA h, and fraction of zinc consumed up to 5×10^{-5}.

1. Introduction

Due to the rising cost of fuel and the environmental pollution resulting from the burning of fuel, there is urgent need for clean and renewable energy, such as that generated by batteries. Due to their limited energy density, conventional batteries (which are quite small) cannot provide large amounts of energy. As a result, batteries are mostly used as power sources for small devices, such as digital cameras.

A battery consists of an anode (the electrode which is an electronic conductor and which undergoes chemical oxidation during the discharge of the battery) and a cathode (the electrode which is an electronic conductor and which 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. The anode and cathode must be separated by an electrolyte, which is an ionic conductor, but is an electronic insulator.

Batteries and fuel cells suffer from: (i) the safety (leakage) and environmental problems associated with the electrolyte in the usual case that the electrolyte is a liquid, (ii) the poor interface between the electrodes (anode/cathode) and the electrolyte and the inadequate room-temperature ionic conductivity of the electrolyte in case that the electrolyte is a solid, and (iii) 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. The ionic conductivity of an electrolyte should be sufficiently high, so that the electrical resistance associated with the electrolyte in the battery is sufficiently low. This resistance contributes significantly to the internal resistance of a battery. A low resistance enables a battery to carry a high current.

There are two classes of electrolyte, namely 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 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 shortcoming of liquid electrolytes is associated with the tendency of leakage of the liquid electrolyte from the battery, either during use or after disposal, and the environmental pollution that results from this leakage. Examples of liquid electrolytes are aqueous solutions with dissolved salts (e.g., potassium hydroxide). Water is itself an electrolyte. To increase the ionic conductivity of water, a salt is usually dissolved in the water. 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.

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A novel class of batteries uses the pore solution in cement as the electrolyte. Cement-based batteries that utilize a cement-based electrolyte have been disclosed by Burstein and Speckert [1] and Sakai et al. [2]. The use of an inexpensive and abundant material, such as cement, for batteries enables the development of large batteries. Furthermore, by incorporating the cement-based battery as a part of a structure, the battery does not consume extra space (since the structure is present anyway) and that potentially provides large amounts of energy. In other words, the battery becomes integrated with a structure. A large battery is advantageous for providing or storing a large amount of energy.

A monolithic cement-based battery can be portable or be fixed at a location. Cement-based 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 black-outs. The ability to generate energy provides a new level of smartness to smart structures.

Burstein and Speckert [1] used aluminum (a 5-mm diameter cylinder, which dissolves during discharge) as the anode, water (which is reduced to hydrogen) as the cathode, steel as the cathode electrocatalyst, and the pore solution in cement paste (set, without aggregate) as the electrolyte for a battery that can be operated at a low current density (0.25 $\mu A/cm^2$) and a low power output per unit area (0.1 $\mu W/cm^2$) in the essential absence of oxygen (as in deep sea oil wells and pipelines). The dissolution of the aluminum anode during discharge caused the anode-electrolyte interface to degrade during discharge. It is well-known that aluminum dissolves in cement, so a cement-based material containing an aluminum filler becomes porous and loses its mechanical properties as time progresses.

Sakai et al. [2] used zinc as the anode, manganese dioxide as the cathode, and water (in fresh concrete, not cured) as the electrolyte of a battery that provides power during concrete construction. The mobility of water decreases greatly during setting. Thus, the use of the pore solution in set cement as the electrolyte is more challenging than the use of the pore solution in fresh cement [2] as the electrolyte. In spite of the challenge, the use of the pore solution in set cement as the electrolyte greatly widens the applicability of the battery technology.

Charkley [3] used cement as an additive to a zinc anode, which is for use in a battery that does not involve cement or its the pore solution as the electrolyte. Thus, Ref. [3] is not really relevant.

Asakura [4] and Kawamata et al. [5] reported the use of zinc particles (together with carbon particles) in cement for forming sacrificial anodes for the corrosion protection of steel. This technology is distinct from that of cement-based batteries.

Matsuura et al. [6] reported the use of manganese dioxide in cement for enhancing the rate of setting and curing. This technology is also distinct from that of cement-based batteries.

The use of the pore solution in cement as an electrolyte is attractive due to the environmental compatibility of cement. In addition, the fact that water is naturally contained in set cement means that the cement does not need to be packaged in a container. Therefore, the use of the pore solution of cement as an electrolyte provides the abovementioned advantages of a liquid electrolyte while avoiding the abovementioned disadvantages of a liquid electrolyte. In addition, the use of the pore solution of cement as an electrolyte provides the abovementioned advantages of a solid electrolyte while avoiding the abovementioned disadvantages of a solid electrolyte.

The present paper is mainly aimed at: (i) overcoming the abovementioned limitations of the prior art on cement-based batteries, (ii) developing a cement-based battery in the form of a monolithic device, with anode, cathode and electrolyte all based on set cement, the pore solution of which is the electrolyte, (iii) developing a cement-based material involving zinc as the active component in the anode and manganese dioxide as the active component in the cathode, and (iv) providing the initial science base for the design of cement-based batteries.

2. Concept

In the cement-based battery of this paper, the anode, cathode and electrolyte components all involve cement as the continuous matrix. In contrast, the anode, cathode and electrolyte of cement batteries of the prior art 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. In the cement batteries of Burstein and Speckert [1], the anode is aluminum metal, the cathode is water, and the electrolyte is the pore solution in cement. 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 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 cement-based battery of this paper does not require a container. It is in the form of a cement-matrix monolith. Although water is present, it is held inside the cement. The monolithic structure results in good mechanical integrity, good handle ability 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.

The cement-based battery of this paper is in the form of a slab (Fig. 1), with the anode component, electrolyte component and cathode component in the form of contiguous layers in the plane of the slab. The pore solution in the cement constituent provides the electrolyte function. The anode component comprises cement and an electrochemically active component. The cathode component comprises cement and another electrochemically active component. The anode component and the cathode component are completely separated by the electrolyte component, which is based on cement. The active component in the anode component is dispersed in the anode component; the active component in the cathode component is dispersed in the cathode component.

The battery is in the shape of a slab (e.g., a tile) in this work, but it is not restricted to this geometry. This shape may be used for portable batteries as well as batteries that are fixed at particular locations. The portability widens the applications. In addition, the small size of a portable battery widens the range of processing methods that can be utilized in manufacturing the battery.

The electrolyte (the pore solution in cement) in the cement-based battery of this paper is spatially distributed. The cement-based anode, electrolyte and cathode may be integrated by their layer-by-layer casting (Fig. 1). Whether the anode or the cathode is at the bottom of the battery does not affect battery operation. However, for mechanical stability enhancement, it is preferred that the electrode that is higher in density be at the bottom. The electrolyte layer is preferably thin in order to reduce the resistance.

Cement is itself an ionic conductor (due to the pore solution in the cement), so the use of the pore solution in cement as an electrolyte does not require a conductivity-enhancing additive. However, because of the discontinuity of the active particles in an electrode, an electrically conductive additive, such as carbon black, may be used. In particular, an active component that is electronically nonconductive (e.g., manganese dioxide) requires the use of an electronically conductive additive (e.g., carbon black). Carbon black is in the form of nanoparticles that form aggregates. Due to this morphology, carbon black is squishable (highly compressible). Because of its small particle size, carbon black is effective for filling small spaces, such as the space between adjacent active particles.

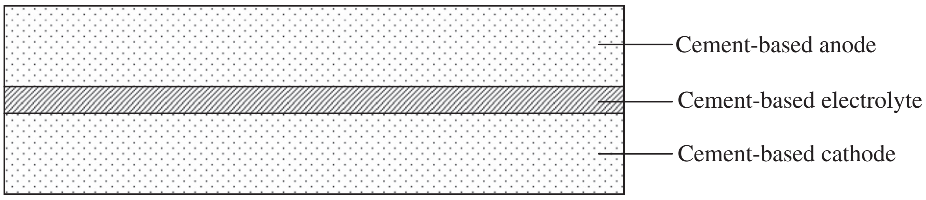

Fig. 1. Schematic illustration of a battery of this paper, with cement as the continuous constituent (matrix) in the cathode, electrolyte and anode regions.

In case that the electrode active component is electronically conductive (e.g., zinc), the use of an electronically conductive additive may not be necessary. Nevertheless, the use of an electronically conductive additive in this case still helps the electrical connectivity, because the quality of the electrical contact between adjacent conductive active particles may not be sufficient without the conductive additive.

The proportion of electronically conductive additive in an electrode needs to be sufficient for helping 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. The optimum proportion of conductive additive depends on the particle size and aspect ratio of the active component. The smaller is the particle size, the larger is the proportion of conductive additive needed to attain electrical connectivity, due to the larger amount of particle–particle interface. The higher is the aspect ratio of the particles, the lower is the proportion of conductive additive needed to attain electrical connectivity.

A material may react with moisture, oxygen or other ingredients in the environment and thus become covered by a thin layer of the reaction product. In case that the material is conductive particles (e.g., zinc) and the reaction product is nonconductive (e.g., zinc oxide), the reaction product is detrimental to the electrical connectivity of the particles. In case of zinc particles, the removal of the oxide coating may be achieved by washing with acetic acid prior to incorporation in cement. Following this washing, the particle should be rinsed with a volatile liquid (e.g., ethanol).

The ionic conductivity of cement may be increased by dissolving a water-soluble salt (such as sodium chloride and calcium chloride) in water prior to using the water in the cement mix. However, no salt is used in this work.

The appropriate thickness of the anode or cathode layer is governed by the amount of active component, which affects the capacity of the battery. The ratio of the amount of active component 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 cement-based batteries may be similarly formed in the same general location. A cement-based battery stack may thus be formed by electrically connecting components in series.

As cement is the matrix in both anode and cathode, the anode active phase is in direct contact with the electrolyte throughout the anode region and the cathode active phase is in direct contact with the electrolyte throughout the cathode region – not just at a localized interface between an electrode and the electrolyte (e.g., the localized interface between an anode cylinder and the cement-based electrolyte in the batteries disclosed by Burstein and Speckert [1]). Thus, the area of the interface between the electrolyte and either electrode is large. In general, a large interface area is attractive for battery operation at a high current (i.e., a high rate) and for enhancing the thorough use of the active components during battery operation. In addition, a large interface area is attractive for diminishing the resistance associated with the interface.

As for conventional batteries, a cement-based battery may be rechargeable, 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 a structure.

An electrochemical cell works because of chemical dissimilarity between the anode and cathode regions of the cell. A cell can achieve the dissimilarity by involving different compositions for the anode and the cathode. Another method for a cell to achieve the dissimilarity involves different compositions of electrolyte in the anode and cathode regions of the cell.

3. Methods

3.1. Materials

The cement used was Portland cement (Type I) from Lafarge Corp. (Southfield, MI, USA). The water/cement ratio was 0.35, unless noted otherwise.

The zinc particle used as the active component in the anode was zinc dust 122 from Horsehead Corp. (Monanca, PA, USA). It contained 99.3% zinc. The median particle size was 7 μm. The density was 7.452 g/cm^3. Immediately prior to use, the surface of the zinc dust was cleansed of its native oxide by acetic acid washing, followed by ethanol rinsing. Unless noted otherwise, treated (cleansed) zinc dust was used.

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, USA). The powder comprised the following principal components: MnO_2 82–85%, quartz 1–3%, and barium compounds 1–2%. The average particle size was 40 μm. The density was 5.02 g/cm^3.

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

A high-range water-reducing admixture (Glenium 3000 NS, Degussa Admixtures, Cleveland, OH) that was based on polycarboxylate chemistry was used in the amount of 1.0% by mass of cement, unless noted otherwise.

Distinct specimens of anode, cathode and electrolyte were prepared and tested for the purpose of developing the formulations of the anode and cathode. For each formulation, three specimens were tested after curing in terms of the electrical resistivity and the relative dielectric constant. Every specimen for resistivity measurement had dimensions 62 × 13 × 12.5 mm, as prepared by using a steel mold. Every specimen for relative dielectric constant measurement had diameter 12 mm and height 1.5 mm, as prepared by using a cylindrical silicone mold.

Although the workability was not measured, some mixes were found during mixing to be unacceptable in workability. A mix that was low in workability tended to result in a high resistivity, due to the large amount of air voids in the specimen.

The specimen preparation involved the following steps. The surface of the mold cavity was oiled for the purpose of facilitating demolding. Weighed amounts of cement, active electrode component (zinc or MnO_2) and carbon black (if applicable) were combined in a ceramic bowl and manually mixed for 3 min by using a spatula. The water reducing agent and water (0.35 of the cement weight for either electrode component, and 0.40 of the cement weight for the electrolyte component) were added and the mixture was blended. The mixture was poured into a mold. The mold was placed in a moisture box with 100% relative humidity. The specimen was demolded after 24 h and then returned to the moisture box for curing for a controlled number of days.

3.2. Anode/cathode/electrolyte component specimen testing methods

The anode, cathode and electrolyte component specimens were separately tested in terms of their electrical resistivity and relative dielectric constant.

3.2.1. Electrical resistivity measurement method

The electrical resistivity is a basic property of an electrode or an electrolyte. An electrode needs to be an electronic conductor, whereas an electrolyte needs to be an ionic conductor.

For electrical resistivity measurement of anode, cathode and electrolyte component specimens, four electrical contacts were applied to each specimen. The four contacts were at four parallel planes that were perpendicular to the direction of resistance measurement. Each contact that was not at an end surface was around the whole perimeter of the specimen. In accordance with the four-probe method, the outer two contacts were for passing current, while the inner two contacts were for voltage measurement (Fig. 2). The voltage contacts were electronic conductors in the form of silver paint in conjunction with copper wire. The current contacts were of two forms, namely electronic conductor (silver paint in conjunction with copper wire) and ionic conductor (an aqueous solution containing 0.33 mol/liter of KOH and 0.13 mol/liter NaOH, with the solution held in a sponge and with a copper foil inserted in the sponge to provide electrical connection to the electronics, Fig. 3). Each current contact in the form of an electronic conductor was around the whole perimeter at a plane which was at a distance from the end surface. Each current contact in the form of an ionic conductor was at an end surface perpendicular to the direction of resistance measurement, such that it covered the entire end surface. Each specimen was subjected to both forms of resistivity measurement.

An electronic conductor as the electrical contact does not allow ions to be injected into the specimen, whereas an ionic conductor as the electrical contact does not allow electrons to be injected into the specimen. Thus, an electronic conductor as the current contact tends to promote electronic conduction, whereas an ionic conductor as the current contact 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.

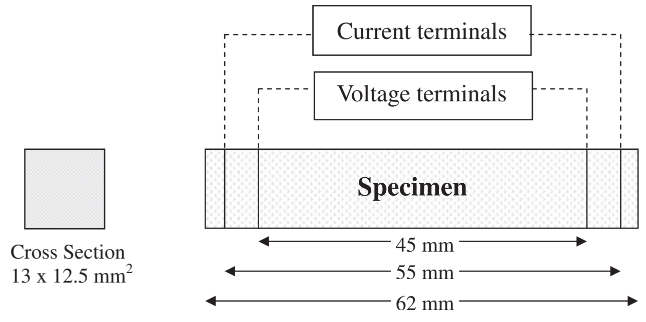

Fig. 2. Four-probe configuration for electrical resistivity measurement that involves current contacts in the form of electronic conductors (silver). The specimen is a cement-based anode, cathode or electrolyte.

The electrical resistance was measured by using a precision multimeter (Model 2001, Keithley, Cleveland, OH) operated in the four-probe configuration. The specimen was of length 62 mm in the direction of the resistance measurement. The two voltage contacts, which were symmetrically positioned with respect to the midpoint of the length, were 45 mm apart (Fig. 2 and 3). The cross-sectional dimensions were 13 × 9 mm. The resistivity was given by the product of the resistance and the cross-sectional area, divided by the distance between the two voltage contacts.

3.2.2. Relative dielectric constant measurement method

The relative dielectric constant relates to the extent of ion movement in response to an applied AC electric field. Its value is preferably high for an electrolyte. 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 RLC meter (Quadtech Model 7600). The parallel plates (electrodes) sandwiching the specimen were copper discs of diameter 12 mm and thickness 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, the relative dielectric constant κ was calculated using the equation

$$\kappa = \frac{Cd}{\varepsilon_0 A} \tag{1}$$

where $d = 1.55$ mm was the distance between the two electrodes, $A = 113.09\ \text{mm}^2$ was the contact area, and $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m is the permittivity of free space. The frequencies used were 1 kHz and 1 MHz; the voltages used were 1.000 V and 100 mV.

3.3. Formulation development

This section pertains to the development of the formulations of the cement-based anode, cathode and electrolyte components.

3.3.1. Cement-based anode formulation development

In order to show the procedure of formulation development, cement-based anode formulations investigated prior to arriving at the chosen formulation are also described. In this section, the curing period was 7 days. The resistivity was measured by using current contacts that were in the form of an electronic conductor.

The addition of carbon black greatly reduced the workability of the mix, so the proportion of water reducing agent was 1% by mass of cement when carbon black was absent and 2% by mass of cement when carbon black was present. The addition of carbon black decreased the resistivity from 10^8 to $10^6\ \Omega$ cm, as shown for untreated zinc in the anode. The zinc surface treatment (cleansing) similarly decreased the resistivity from 10^8 to $10^6\ \Omega$ cm, as shown in the absence of carbon black. In the presence of carbon black, the treatment of zinc decreased the resistivity from 10^6 to $10^3\ \Omega$ cm. The addition of carbon black to the anode with treated zinc similarly decreased the resistivity from 10^6 to $10^3\ \Omega$ cm. Thus, both zinc surface treatment and carbon black are needed for attaining the low resistivity of $10^3\ \Omega$ cm. Comparison of Formulations 1 and 2 (both with treated zinc and carbon black) in Table 1 shows

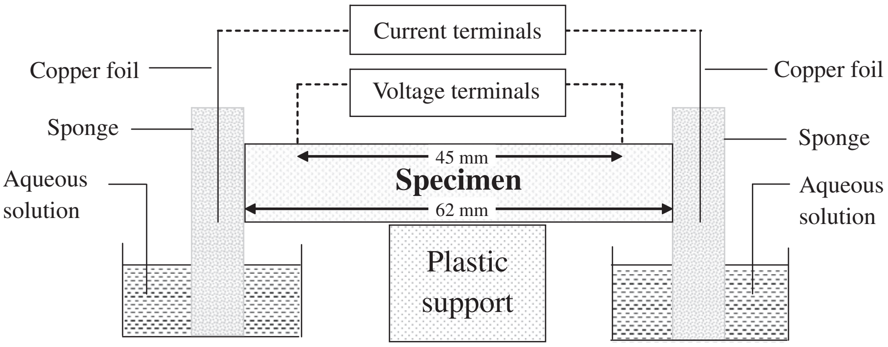

Fig. 3. Four-probe configuration for electrical resistivity measurement that involves current contacts in the form of ionic conductors (an aqueous solution).

that the former gave a lower resistivity, due to its higher zinc content. Therefore, Formulation 1 is adopted.

3.3.2. Cement-based cathode formulation development

The goal of this section is to maximize the MnO_2/carbon black ratio and to achieve a low resistivity (obtained by using current contacts that were in the form of an electronic conductor). The MnO_2 (with carbon black in the amount of 1% by mass of cement) was more effective than untreated zinc (with carbon black in the larger amount of 1.2–2.4% by mass of cement) in decreasing the resistivity. The resistivity of the MnO_2 cathode decreased monotonically as the carbon black proportion increased from 1% to 4% by mass of cement. With the highest carbon black proportion of 4% by mass of cement, the resistivity was sufficiently low (Table 2). Further increase of the carbon black proportion caused the workability to be unacceptably low and caused the resulting composite to be fragile. Decrease of the MnO_2 proportion had only a small effect on the resistivity (Table 2). Nevertheless, Formulation 3 (Table 2) gave the lowest resistivity and is therefore adopted.

3.3.3. Cement-based electrolyte component formulation development

As in the anode and cathode formulations, the water reducing agent was used in the amount of 1% of mass of cement. However, the water/cement ratio was increased from 0.35 to 0.40 for the purpose of decreasing the resistivity (obtained by using current contacts that were in the form of an ionic conductor), which is important for the electrolyte component. The chosen electrolyte component formulation is described in Table 3. The electrolyte component contained 28 wt.% water.

4. Evaluation of anode/cathode/electrolyte components

4.1. Electrical resistivity evaluation of the selected anode/cathode/electrolyte component formulations at 7 days of curing

For the purpose of characterization, the resistivities measured by using the ionic and electronic forms of current contacts were measured for the preferred anode, cathode and electrolyte component formulations described in Sections 3.3.1–3.3.3 respectively and summarized in Table 4. The specimens were separately prepared, as described in Section 3.1. The curing period was 7 days.

The resistivity obtained by using electronic contacts was much lower for the anode and cathode components than the electrolyte component, whereas that obtained by using ionic contacts was lower for the electrolyte component than the anode or cathode component (Table 5). This means that the electrode components were better electronic conductors than the electrolyte component, whereas the electrolyte component was a better ionic conductor than either electrode component.

The resistivities obtained by using electronic and ionic forms of current contacts were similar for each electrode. This suggests that, for either electrode, the conduction due to electrons (associated with carbon black in the cathode and associated with both carbon black and zinc in the anode) was substantial, whether the contacts were electronic or ionic. In contrast, for the electrolyte component, the resistivity measured by using ionic contacts was much smaller

Table 1
Cement-based anode formulations (with treated zinc and carbon black) and electrical resistivity (last row) measured using electrical contacts in the form of an electronic conductor. The water reducing agent (WR) was used in the amount of 2% by mass of cement.

Formulation 1	Formulation 2
Cement: 50.0 g	Cement: 50.0 g
Zinc: 15.0 g (5.0 vol.%)	Zinc: 6.0 g (2.0 vol.%)
Carbon black: 1.2 g	Carbon black: 1.2 g
WR: 1.0 g	WR: 1.0 g
Water: 17.5 g	Water: 17.5 g
1300 Ω cm (±8%)	9800 Ω cm (±10%)

Table 2
Cement-based cathode formulations (with MnO_2 and carbon black) and electrical resistivity (last row) measured using electrical contacts in the form of an electronic conductor. The proportion of carbon black was 4% by mass of cement. The proportion of the water reducing agent (WR) was 2% by mass of cement.

Formulation 1	Formulation 2	Formulation 3
Cement: 50.0 g	Cement: 50.0 g	Cement: 50.0 g
MnO_2: 30.0 g (14.4 vol.%)	MnO_2: 25.0 g (12.0 vol.%)	MnO_2: 20.0 g (9.6 vol.%)
Carbon black: 2.0 g	Carbon black: 2.0 g	Carbon black: 2.0 g
WR: 1.0 g	WR: 1.0 g	WR: 1.0 g
Water: 17.5 g	Water: 17.5 g	Water: 17.5 g
2200 Ω cm (±20%)	2700 Ω cm (±30%)	1990 Ω cm (±3%)

Table 3
Electrolyte formulation (WR = water reducing agent).

Cement: 50.0 g
WR: 0.5 g
Water: 20.0 g

Table 4
Preferred formulations for the cement-based anode, cathode and electrolyte. (WR = water reducing agent).

Anode formulation	Cathode formulation	Electrolyte formulation
Cement: 50.0 g	Cement: 50.0 g	Cement: 50.0 g
Zinc: 15.0 g (5.0 vol.%)	MnO_2: 20.0 g (9.6 vol.%)	–
Carbon black: 1.2 g	Carbon black: 2.0 g	–
WR: 1.0 g	WR: 1.0 g	WR: 0.5 g
Water: 17.5 g	Water: 17.5 g	Water: 20.0 g

Table 5
Electrical resistivity (Ω cm) measured by using current contacts in the form of electronic or ionic conductors for selected formulations of the anode, cathode and electrolyte at 7 days of curing.

Current contacts	Anode	Cathode	Electrolyte
Electronic	1200 (±10%)	1170 (±8%)	2800 (±11%)
Ionic	1300 (±25%)	1100 (±12%)	910 (±12%)

than that obtained by using electronic contacts, indicating that ionic conduction dominated in the electrolyte component.

4.2. Cement-based anode/cathode/electrolyte component characterization at 28 days of curing

In this section, the curing age was 28 days. The testing was conducted in terms of the electrical resistivity (using both current contacts in the form of ionic and electronic conductors) and the relative dielectric constant.

4.2.1. Electrical resistivity at 28 days of curing

The resistivity results at 28 days of curing are shown in Table 6, with comparison with the corresponding results at 7 days of curing. All resistivities (whether anode component, cathode component or electrolyte component) were increased upon increasing the curing age from 7 to 28 days. This is expected, due to the decrease in the amount of mobile water as curing progresses. At both 7 and 28 days, the resistivity of the electrolyte component, as obtained by using ionic contacts, was lower than that obtained by using electronic contacts. At both ages, the resistivity of the electrolyte component was higher than that of the anode/cathode component when electronic contacts were used, whereas the resistivity of the electrolyte component was lower than that of the anode/cathode component when ionic contacts were used.

4.2.2. Relative dielectric constant at 28 days of curing

Tables 7 and 8 show the values of the relative dielectric constant (along with the capacitance values) for series and parallel configurations respectively. The 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 much higher for the electrolyte component than the anode or cathode component and the values were similar for the anode and cathode components. The high value for the electrolyte component supported the effectiveness of the electrolyte component.

5. Cement-based battery design, preparation and testing methods

5.1. Cement-based battery design

Table 6
Electrical resistivity (Ω cm) measured by using current contacts in the form of electronic or ionic conductors for selected formulations for the anode, cathode and electrolyte at 7 and 28 days of curing.

Current contacts	Curing time (days)	Anode	Cathode	Electrolyte
Electronic form	7	1200 (±10%)	1170 (±8%)	2800 (±11%)
	28	2000 (±15%)	2200 (±8%)	3500 (±8%)
Ionic form	7	1300 (±25%)	1100 (±12%)	910 (±12%)
	28	2000 (±20%)	1500 (±12%)	1100 (±12%)

Table 7
The relative dielectric constant κ of anode, cathode and electrolyte at 28 days of curing, as obtained from the capacitance based on the series configuration of the resistor and capacitor in the equivalent circuit.

Voltage amplitude	100 mV		1 V	
Frequency	1 kHz	1 MHz	1 kHz	1 MHz
Anode	14 (±20%)	11 (±12%)	12 (±19%)	9 (±22%)
Cathode	13 (±14%)	11 (±18%)	10 (±20%)	10 (±36%)
Electrolyte	24 (±23%)	19 (±14%)	19 (±11%)	15 (±29%)

Table 8
The relative dielectric constant κ of anode, cathode and electrolyte at 28 days of curing, as obtained from the capacitance based on the parallel configuration of the resistor and capacitor in the equivalent circuit.

Voltage amplitude	100 mV		1 V	
Frequency	1 kHz	1 MHz	1 kHz	1 MHz
Anode	14 (±20%)	11 (±10%)	12 (±21%)	8 (±23%)
Cathode	13 (±16%)	11 (±18%)	10 (±18%)	10 (±30%)
Electrolyte	24 (±30%)	18 (±14%)	19 (±10%)	15 (±28%)

This section describes the design of cement-based batteries, with consideration of the battery configuration and dimensions. The composition of each battery component is described in Section 3.3.

A cement-based battery was a stack of anode, electrolyte and cathode components that had been cured simultaneously, as illustrated in Fig. 1. The base of the stack had dimensions 80 mm × 40 mm. The stack geometry is suitable for structures in the form of slabs and is attractive for the large slab area, which helps provide a low resistance. (The resistance is inversely proportional to the area.)

The chemical reactions for a Zn–MnO_2 electrochemical cell are shown below.

$$\text{Anode}: \mathrm{Zn} + 2\mathrm{OH}^- \rightarrow \mathrm{ZnO} + \mathrm{H_2O} + 2\mathrm{e}^-$$

$$\text{Cathode}: 2\mathrm{MnO_2} + \mathrm{H_2O} + 2\mathrm{e}^- \rightarrow \mathrm{Mn_2O_3} + 2\mathrm{OH}^-$$

From these reactions, the atomic ratio of Zn (in anode) to MnO_2 (in cathode) should be 1:2, if both active components are completely consumed by the reaction. The atomic mass of zinc is 65.39 g/mol; the atomic mass of MnO_2 is 84.93 g/mol. Thus the corresponding mass proportion is Zn:MnO_2 = 65.39:168.78. The proportion of Zn in the cement-based anode is 30% by mass of cement; the proportion of MnO_2 in the cement-based cathode is 40% by mass of cement (Section 3.3). Let the weight of cement in the anode and cathode be X and Y respectively. Hence,

$$\frac{X \times 30\%}{Y \times 40\%} = \frac{65.39}{168.78} \Rightarrow \frac{X}{Y} = \frac{0.516}{1} \tag{2}$$

Thus, an anode/cathode thickness ratio of about 0.5 is preferred. The electrolyte component layer should be as thin as possible, provided that the anode and cathode components do not contact one another and that the cement mix for the electrolyte component is fluid enough to spread thin.

Batteries with the same component compositions but different dimensions were prepared and tested, as summarized below. Battery 1 was the thickest; Battery 3 was the thinnest; Battery 2 was intermediate in thickness. Three batteries of each size were prepared at the same time.

Battery 1 had component thicknesses a = 12 mm, b = 24 mm and c = 4 mm, where a is the anode layer thickness, b is the cathode layer thickness and c is the electrolyte component thickness. Battery 2 had dimensions a = 4 mm, b = 8 mm and c = 2 mm. Bat-

Table 9
Formulation of batteries. WR = water reducing agent. Volume percentages are relative to the volume of the anode/electrolyte/cathode.

Battery No.	Anode	Electrolyte	Cathode
1	Cement: 48 g	Cement: 15 g	Cement: 93 g
	Zinc: 14.4 g (5.0 vol.%)	–	MnO_2: 37.2 g (9.6 vol.%)
	Carbon black: 1.2 g	–	Carbon black 3.7 g
	Water: 16.8 g	Water: 6 g	Water: 33.6 g
	WR: 1.0 g	WR: 0.15 g	WR: 1.8 g
2	Cement: 16 g	Cement: 5.0 g	Cement: 31 g
	Zinc: 4.8 g (5.0 vol.%)	–	MnO_2: 12.4 g (9.6 vol.%)
	Carbon black: 0.384 g	–	Carbon black: 1.24 g
	Water: 5.6 g	Water: 2.0 g	Water: 10.85 g
	WR: 0.32 g	WR: 0.5 g	WR: 0.62 g
3	Cement: 10.0 g	Cement: 3.0 g	Cement: 19.4 g
	Zinc: 3.0 g (5.0 vol.%)	–	MnO_2: 7.8 g (9.6 vol.%)
	Carbon black: 0.24 g	–	Carbon black: 0.8 g
	Water: 3.5 g	Water: 1.2 g	Water: 6.8 g
	WR: 0.2 g	WR: 0.3 g	WR: 0.4 g

tery 3 had dimensions $a = 2.5$ mm, $b = 5$ mm and $c = 1$ mm. The amounts listed in Table 9 for each battery are those for making one battery of the corresponding dimensions.

5.2. Cement-based battery preparation

Cement-based batteries were prepared according to the formulations described in Table 9. The preparation methods are described below.

High-density polyethylene molds were used to make battery specimens. The lateral dimensions of the batteries were 80 mm × 40 mm (Battery 1), 80 mm × 14 mm (Battery 2), and 80 mm × 8.5 mm (Battery 3). Batteries 1–3 are as described in Section 5.1.

The procedure of battery preparation involved the following steps. The mixes for the cathode, electrolyte and anode components were separately prepared as described in Section 3.1. A rotary mixer with a flat beater was used. The cathode component mix was poured into a mold cavity. Immediately afterward, half of the electrolyte component mix was poured on the surface of placed cathode mix. A piece of one-ply absorbent paper (i.e., tissue paper) (Adept Wipes, HLO Enterprises, San Francisco, CA) was placed on the electrolyte component mix in the plane of the specimen. The other half of the electrolyte component mix was immediately poured on the placed paper, such that the paper became entirely covered by the electrolyte component mix. Immediately afterward, the anode component mix was poured on the surface of the placed electrolyte component layer. The mold was placed in a moisture box with 100% relative humidity. After 24 h, the specimen was demolded and then returned to the moisture box. The specimen was kept in the moisture box for 27 (or 6) more days for a total of 28 (or 7) days of curing.

The addition of the piece of paper within the electrolyte component layer was needed to avoid fracture within the electrolyte component during curing. The fracture separated the specimen into two parts and was due to shrinkage-induced stresses. The fracture path was within the electrolyte component layer. The irregularity in the path is due to the fact that the electrolyte component layer was not flat. The piece of paper reduced the shrinkage in the electrolyte component, while the active particles reduced the shrinkage in the anode and cathode components. Without the piece of paper, the imbalanced shrinkage of the electrolyte component compared to the electrode components caused fracture at the electrolyte component layer.

5.3. Cement-based battery testing methods

This section describes the methods of testing cement-based batteries fabricated as described in Section 5.2. After the desired curing time, electrical contacts were applied to the top and bottom surfaces of each battery slab for the purpose of electrical testing.

Every cement-based battery was subjected to an open-circuit voltage measurement following by a constant-current discharge test. Before the open-circuit voltage measurement and after the discharge testing, DC electrical resistance measurement was performed in the direction perpendicular to the plane (layers) of the battery. All electrical contacts were electronic conductors, namely silver paint in conjunction with copper wire. From the measured resistance, the resistivity of the overall battery in the direction perpendicular to the plane of the battery was calculated. All the measurements were performed on batteries in the wet state, i.e., batteries were tested right after having been taken out of the moisture box.

For both discharge testing and resistivity measurement, four electrical contacts were used, with two contacts on each of the two opposite 80-mm long surfaces of the battery. The two contacts on a surface were in the form of two rectangular loops, both of which were centered with respect to the center of the specimen surface. Both loops were smaller than the specimen surface dimensions, such that one loop was smaller than the other and lied within the boundary of the other. All electrical contacts were made with silver paint in conjunction with copper wire. The two loops (together with their associated silver paint) on a surface did not contact one another. For the open-circuit voltage measurement, the inner loop contact on each of the two opposite surfaces was used.

Each cement-based battery was subjected to a constant-current discharge test. At a controlled value of the current, the running voltage was measured as a function of the discharge time until the voltage had dropped to zero. During battery discharge, a constant current, as controlled by a DC current source, was passed from the cathode to the anode, using the outer of the two loop contacts at each electrode. At the same time, the running voltage was measured across the two electrodes, using the inner one 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 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 is attractive for promoting uniform current density.

A DC current source (2400 Series, Keithley, Cleveland, OH) was used to provide a constant current, which was in the range from 5 to 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 current source provided a DC current. The running voltage of the battery was measured by using a precision multimeter (Model 2001, Keithley, Cleveland, OH). 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 failed to function, the current source supplied a DC current and the voltage measured on the multimeter would be negative.

6. Cement-based battery performance

6.1. Cement-based battery discharge performance at 7 days of curing

Batteries 1–3, as described in Section 5.1, were tested at 7 days of curing. Let ρ_1 and ρ_2 denote the resistivity before and after discharge respectively; let V_{oc} denote the open-circuit voltage; and let f denote the fraction of zinc atoms consumed by the discharge reaction.

A relatively low current was chosen for testing Battery 1. Fig. 4 shows the discharge curves at a current of 80 μA and 100 μA of two specimens of Battery 1 at 7 days of curing. The discharge capacities were very low, with a discharge life of only 617 s and 308 s for a current of 80 μA and 100 μA respectively, as shown in Table 10.

Fig. 5 shows four specimens of Battery 2 (thinner than Battery 1) under discharge at 60, 80, 100 and 120 μA respectively. These four batteries worked much better than the two in Fig. 4 in terms of battery life and running voltage. Comparison of the discharge performance at the four different currents (Table 11) shows that the current of 120 μA was too high for discharging the battery, as shown by the low open-circuit voltage, the low running voltage, the short discharge life and the small fraction of zinc consumed by the discharge.

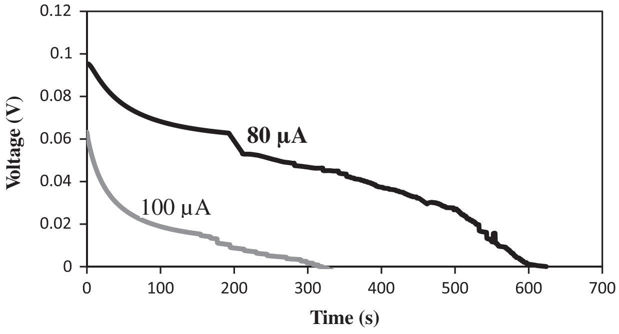

Fig. 4. Constant-current discharge of Battery 1 at 7 days of curing. Battery at 80 μA: $\rho_1 = 53{,}353\ \Omega$ cm; $\rho_2 = 59{,}259\ \Omega$ cm; $V_{oc} = 0.31$ V; $f = 1.14 \times 10^{-6}$; Battery at 100 μA: $\rho_1 = 48{,}234\ \Omega$ cm; $\rho_2 = 49{,}415\ \Omega$ cm; $V_{oc} = 0.29$ V; $f = 7.5 \times 10^{-7}$.

Six specimens of Battery 3 (the thinnest battery) were tested. The average resistivity measured was $1.3 \times 10^7\ \Omega$ cm (±30%). None of these batteries could provide electricity, i.e., no open-circuit voltage was detected, and the voltage measured in constant-current discharge testing at 60 μA and 80 μA was negative. A negative value means that the current source rather than the battery provided the electricity. The failure of Battery 3 was probably due to the inadequate separation of the anode and cathode within the battery.

Among Batteries 1, 2 and 3, Battery 2 (the intermediate size) performed the best. This is because of (i) the excessive thickness of the electrolyte component layer in Battery 1 and the consequent high electrical resistance, and (ii) the inadequate thickness of the electrolyte component layer in Battery 3 and the consequent electrical short-circuiting between the anode and cathode components.

6.2. Cement-based battery discharge performance at 28 days of curing

Two batches of three specimens each were made for Battery 2. The three specimens in a batch were discharged at three different currents, namely 60, 80 and 100 μA.

Fig. 6 shows the constant-current (60 μA) discharge behavior of two specimens from different batches. The specimen from Batch 2 performed better than those of Batch 1 in terms of the open-circuit voltage, the discharge life and the fraction of zinc consumed. The large difference in performance between these two specimens indicates that control of battery performance has not been attained adequately.

As shown in Fig. 7 for constant-current discharge at 80 μA, the specimen from Batch 2 of Battery 2 performed better than that

Table 10
Battery 1 at 7 days of curing discharged at different currents.

Current (μA)	Open-circuit voltage (V)	Discharge life (s)	Capacity (mA h)	Fraction of zinc consumed	Resistivity after discharge (Ω cm)
80	0.31	617	0.014	1.14×10^{-6}	59,259
100	0.29	308	0.0086	7.5×10^{-7}	49,415

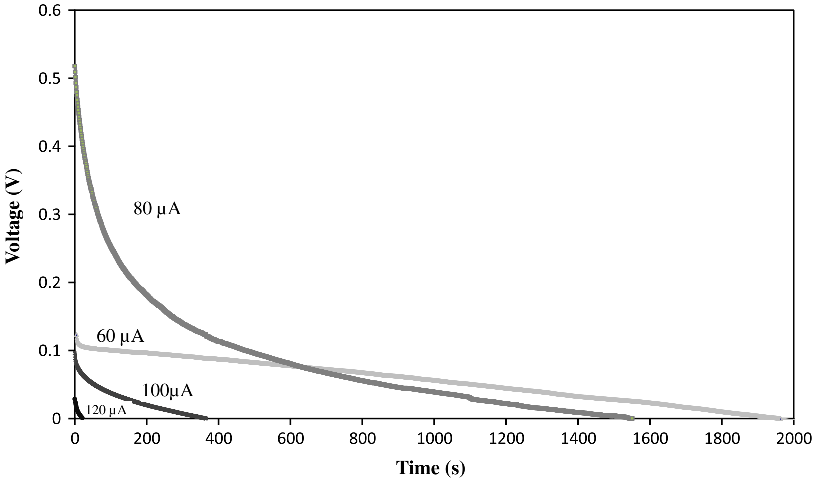

Fig. 5. Constant-current discharge of Battery 2 at 7 days curing. Battery at 60 μA: $\rho_1 = 5376\ \Omega$ cm; $\rho_2 = 10{,}752\ \Omega$ cm; $V_{oc} = 0.21$ V; $f = 2.1 \times 10^{-6}$; Battery at 80 μA: $\rho_1 = 4860\ \Omega$ cm; $\rho_2 = 8640\ \Omega$ cm; $V_{oc} = 0.23$ V; $f = 2.2 \times 10^{-6}$; Battery at 100 μA: $\rho_1 = 4320\ \Omega$ cm; $\rho_2 = 10{,}800\ \Omega$ cm; $V_{oc} = 0.18$ V; $f = 1.1 \times 10^{-5}$; Battery at 120 μA: $\rho_1 = 3430\ \Omega$ cm; $\rho_2 = 9384\ \Omega$ cm; $V_{oc} = 0.19$ V; $f = 1.9 \times 10^{-7}$.

Table 11
Battery 2 at 7 days of curing, discharged at different currents.

Current (μA)	Open-circuit voltage (V)	Discharge life (s)	Capacity (mA h)	Fraction of zinc consumed	Resistivity after discharge (Ω cm)
60	0.21	196	0.0033	2.1×10^{-6}	10,752
80	0.23	396	0.0088	2.2×10^{-6}	8640
100	0.18	1488	0.0413	1.1×10^{-5}	10,800
120	0.19	23	0.00077	1.9×10^{-7}	9384

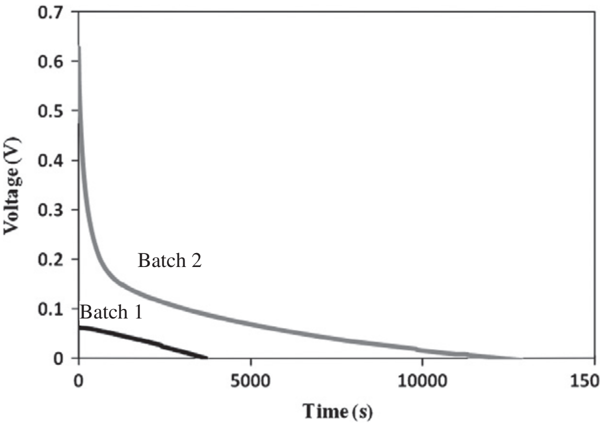

Fig. 6. Constant-current discharge at 60 μA for Battery 2 at 28 days curing. Batch 1: ρ_1 = 9375 Ω cm; ρ_2 = 11,718 Ω cm; V_{oc} = 0.22 V; $f = 1.6 \times 10^{-5}$; Batch 2: ρ_1 = 1631 Ω cm; ρ_2 = 1931 Ω cm; V_{oc} = 0.72 V; $f = 5.2 \times 10^{-5}$.

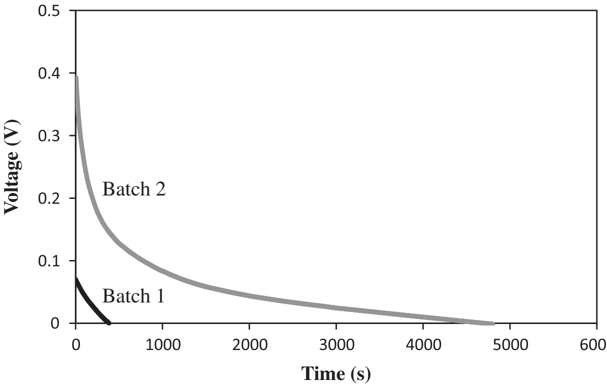

Fig. 7. Constant-current discharge at 80 μA for Battery 2 at 28 days of curing. Batch 1: ρ_1 = 2590 Ω cm; ρ_2 = 3640 Ω cm; V_{oc} = 0.21 V; $f = 2.2 \times 10^{-6}$; Batch 2: ρ_1 = 1922 Ω cm; ρ_2 = 2309 Ω cm; V_{oc} = 0.62 V; $f = 2.7 \times 10^{-5}$.

from Batch 1 of Battery 2, in terms of the open-circuit voltage, discharge life and fraction of zinc consumed.

As shown in Fig. 8 for constant-current discharge at 100 μA, the specimen from Batch 2 of Battery 2 performed better than that from Batch 1 of Battery 2, in terms of the open-circuit voltage, discharge life and fraction of zinc consumed.

At all three currents (60, 80 and 100 μA), the specimens of Batch 2 of Battery 2 performed better than those of Batch 1. It appears that a lower resistivity correlates with better discharge performance. Furthermore, the measured electrical resistivity was lower for Batch 2 than Batch 1.

Comparison of batteries discharged at different currents shows that a higher discharge current resulted in a shorter discharge life (Fig. 9) and a lower discharge capacity (Fig. 10). The latter means that the battery worked better at a lower current. The running voltage at the start of discharge testing did not show a systematic or strong dependence on the current (Fig. 11).

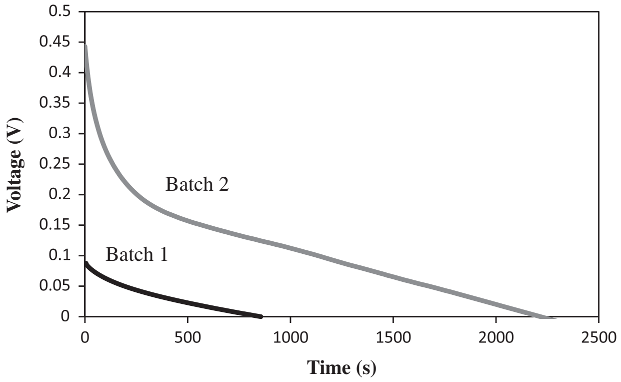

Fig. 8. Constant-current discharge at 100 μA for Battery 2 at 28 days of curing. Batch 1: ρ_1 = 3766 Ω cm; ρ_2 = 4384 Ω cm; V_{oc} = 0.21 V; $f = 2.2 \times 10^{-6}$; Batch 2: ρ_1 = 1687 Ω cm; ρ_2 = 2053 Ω cm; V_{oc} = 0.64 V; $f = 1.6 \times 10^{-5}$.

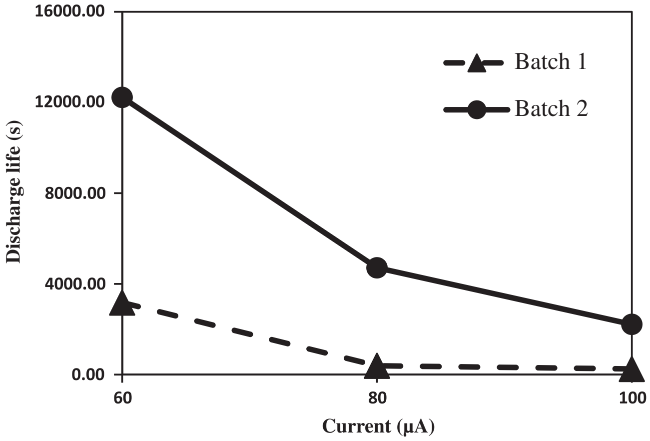

Fig. 9. Cement-based battery discharge life vs. discharge current rate for Battery 2.

Table 12 summarizes the different characteristics of cement-based batteries. The battery in Batch 2 and discharged at 60 μA (current density = 1.88 μA/cm^2) exhibits the highest capacity and the most consumption of zinc. Although 1.88 μA/cm^2 is not a high current density, it is much higher than the value of 0.25 μA/cm^2 previously attained with a cement battery based on the aluminum/water cell [1].

The discharge life of 12,227 s (3.40 h) attained in this work using the battery in Batch 2 and discharged at 60 μA (current density = 1.88 μA/cm^2) is much lower than the life of 600 h for the aluminum/water cement battery discharged at 0.25 μA/cm^2 and reported by Burstein and Speckert [1]. By decreasing the current, the discharge life is expected to increase greatly, as suggested by the data in Fig. 9. Based on the measured discharge life (3.40 h) at a current density of 1.88 μA/cm^2, the discharge life at a current density 0.25 μA/cm^2 is calculated to be at least 26 h. That the life of 26 h is an underestimate is because the capacity increases with decreasing current (Fig. 10).

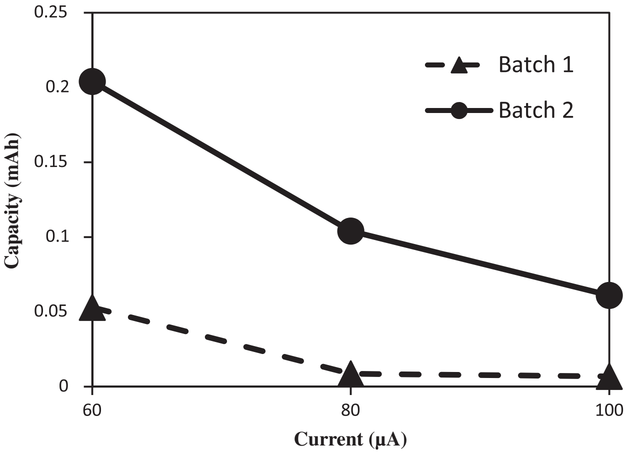

Fig. 10. Cement-based battery capacity vs. discharge current for Battery 2.

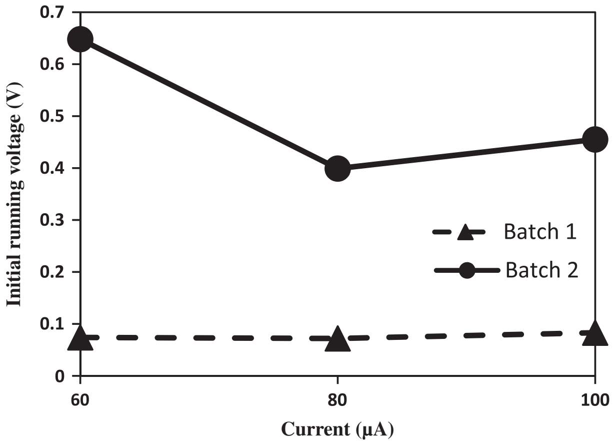

Fig. 11. Cement-based battery initial running voltage vs. discharge current for Battery 2.

The highest running voltage of 0.65 V in this work, as exhibited by the battery in Batch 2 and discharged at 60 μA, is similar to the highest voltage of 0.6 V for the aluminum/water cement battery discharged at 0.25 μA/cm^2 and reported by Burstein and Speckert [1]. The highest initial power output per unit area in this work is 1.42 μW/cm^2, as provided by the battery in Batch 2 and discharged at 100 μA. This value is much higher than the value of 0.1 μW/cm^2 reported by Burstein and Speckert for the aluminum/water cement battery [1]. Thus, the cement-based battery of this work can provide much higher power than the aluminum/water cement battery of Burstein and Speckert.

7. Discussion

The batteries of this work are all much less effective than the commercial alkaline battery, probably due to the poor electrical connectivity of zinc (manganese dioxide) particles in the anode (cathode) and the relatively low ionic conductivity and nonzero electronic conductivity of a set cement-based material. Further development is necessary to make the cement-based battery practical for power generation. Future work on cement-based batteries may involve the following for the purpose of improving the battery performance.

(i) A water-soluble salt (e.g., sodium chloride) may be dissolved in the water prior to mixing in order to enhance the ionic conductivity of the electrolyte component. The additional ions might possibly render the battery functional in the dry state (not just the wet state).
(ii) A polymeric admixture may be added to the cement in order to decrease the electronic conductivity of the electrolyte component.
(iii) In the anode component, the amount of carbon black may be increased without excessively lowering the workability of the mix in order to increase the electrical connectivity of the zinc particles, thereby decreasing the resistivity in the anode component.
(iv) The water/cement ratio in both electrode components and electrolyte component may be increased. With a higher water/cement ratio, the fraction of active components and additives (e.g. carbon black) in the electrodes could be increased without the workability becoming excessively high. Furthermore, more water enhances the ionic conductivity.

8. Conclusion

This work has shown for the first time the basic feasibility of a cement-based battery with the pore solution in set cement as the electrolyte, zinc as the anode, and manganese dioxide as the cathode. This work has also shown the basic feasibility of batteries with the electrolyte being continuous throughout the anode, cathode and electrolyte.

The cement-based battery of this work gives higher current capability and higher power per unit area than that of the prior art that also involves set cement. However, it works only in the wet state.

This work has provided cement-based batteries that are in the shape of a monolithic slab. This shape may be used for portable batteries as well as batteries that are fixed at particular locations.

The cement-based batteries of this work have no aggregate and involve active components (zinc and MnO$_2$) and a conductive additive (carbon black). The conductive additive is present in both anode and cathode. A battery is composed of three layers, namely

Table 12
Performance of two batches of Battery 2 at 28 days of curing under discharge at different constant currents.

Current (μA)	60		80		100	
Current density (μA/cm^2)	1.88		2.50		3.13	
Batch	1	2	1	2	1	2
Open-circuit voltage (V)	0.21	0.72	0.22	0.62	0.21	0.64
Initial running voltage (V)	0.074	0.648	0.072	0.399	0.083	0.455
Initial power output per unit area (μW/cm^2)	0.14	1.22	0.18	1.00	0.26	1.42
Discharge life (s)	3175	12,227	385	4710	247	2215
Capacity (mA h)	0.053	0.204	0.0086	0.105	0.0069	0.0615
Fraction of zinc consumed	1.6×10^{-5}	5.2×10^{-5}	2.2×10^{-6}	2.7×10^{-5}	2.2×10^{-6}	1.6×10^{-5}
Resistivity after discharge (Ω cm)	11,718	1931	3640	2309	4384	2053

cathode component, electrolyte component and anode component. The thickness of the cathode is typically double that of the anode in order to satisfy the requirement of the chemical reaction of the Zn–MnO_2 battery. The three layers are prepared separately by mixing. The battery consists of successively cast and co-cured anode, electrolyte and cathode components. The anode component layer (4 mm thick) comprises cement and zinc particles. The cathode component layer (8 mm thick) comprises cement and manganese dioxide particles. The electrolyte component layer (2 mm thick) is cement with an embedded piece of tissue paper for drying shrinkage control.

The cement-based battery provides open-circuit voltage up to 0.72 V, current up to 120 μA (current density up to 3.8 $\mu A/cm^2$), power output up to 1.4 $\mu W/cm^2$, capacity up to 0.2 mA h, and fraction of zinc consumed up to 5×10^{-5}. The performance is very low compared to commercial alkaline batteries. The resistivity, as measured using electronic contacts, is down to 2000 Ω cm in the direction perpendicular to the plane of the battery. The performance varies among batteries in the same batch and tested under the same condition.

For the cement-based electrolyte, the resistivity measured by using ionic contacts is lower than that measured by using electronic contacts, whereas the resistivity values measured by using electronic and ionic contacts are similar for the cement-based anode and are also similar for the cement-based cathode. Furthermore, the resistivity measured by using electronic contacts is much higher for the cement-based electrolyte than either cement-based anode or cement-based cathode and that measured by using ionic contacts is lower for the cement-based electrolyte than either cement-based anode or cement-based cathode. This indicates the dominance of ionic conduction over electronic conduction in the cement-based electrolyte. In spite of this dominance, the occurrence of some electronic conduction in the cement-based electrolyte is a barrier for the further development of cement-based batteries.

Acknowledgement

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