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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 μ A (current density up to 3.8 μ A/cm²), power output up to 1.4 μ W/cm², capacity up to 0.2 mA h, and fraction of zinc consumed up to 5 × 10⁻⁵.

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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 $(0.25~\mu\text{A/cm}^2)$ and a low power output per unit area $(0.1~\mu\text{W/cm}^2)$ 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 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.

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