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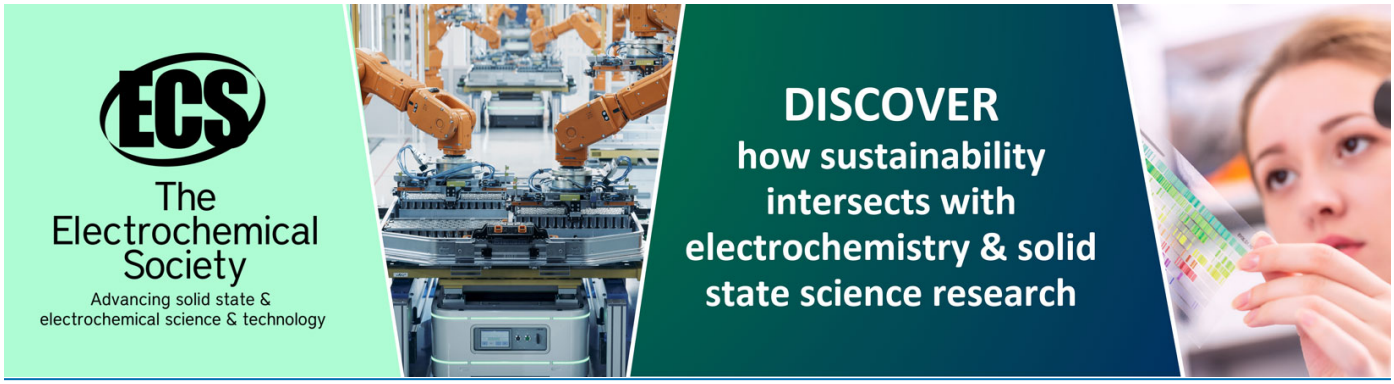

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Cement Based Batteries and their Potential for Use in Low Power Operations

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Abstract. This paper presents the development of an innovative cement-electrolyte battery for low power operations such as cathodic protection of reinforced concrete. A battery design was refined by altering different constituents and examining the open circuit voltage, resistor loaded current and lifespan. The final design consisted of a copper plate cathode, aluminium plate anode, and a cement electrolyte which included additives of carbon black, plasticiser, Alum salt and Epsom salt. A relationship between age, temperature and hydration of the cell and the current it produced was determined. It was found that sealing the battery using varnish increased the moisture retention and current output. Current was also found to increase with internal temperature of the electrolyte and connecting two cells in parallel further doubled or even tripled the current. Parallel-connected cells could sustain an average current of 0.35mA through a 10Ω resistor over two weeks of recording. The preliminary findings demonstrate that cement-based batteries can produce sufficient sustainable electrical outputs with the correct materials and arrangement of components. Work is ongoing to determine how these batteries can be recharged using photovoltaics which will further enhance their sustainability properties.

1. Introduction

Novel battery design is an area that can help ease humanity's dependence on fossil fuels. Research and development focuses on creating higher power storage, greater recharge capacity and extending the life of traditional batteries by adapting their components and materials. The electrolyte of a battery is an ionic conductor but an electronic insulator (resisting the movement of electrons) [1]. Liquid electrolytes are generally favoured due to the high mobility of ions and continuity of interface between electrode and electrolyte. The main issue with liquid electrolyte batteries is the use of toxic materials and their tendency to leak during use or after disposal. Solid electrolytes are not prone to leakage but their ionic conductivity tends to be less than their liquid counterparts and they are more costly. Some examples of solid electrolytes are polymers doped with ions [2-4] or ceramics with ions arranged to

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allow movement [5-7]. Cement is an ionic conductor due to the solution that can be stored in, and travel through, its pores and micro-cracks. This facilitates its potential as a good electrolyte for novel cement battery designs. Cement-based batteries have been sparsely researched, therefore, there have not been many advances in making these batteries more efficient, powerful, long lasting or rechargeable. The work presented here follows on from previous research conducted by the authors in which the cement electrolyte design was refined for highest current (I) and longevity [8]. This paper presents a closer examination of the relationship between temperature and humidity inside the cell and the current output of the refined battery as well as methods of further increasing output by sealing the cells and connecting them in parallel.

Meng *et al*. [1] provided the initial proof of the concept that cement based batteries could be designed to provide a voltage and current output. The design consisted of electrode cement layers with active additives separated by a basic cement electrolyte as shown in figure 1. Examples of successful cement battery development tend to follow the same layered design [9, 10]. However, Burstein *et al*. [11] developed a battery with a steel cathode and an aluminium anode set into a concrete electrolyte which could provide a small current density. Similarly, Ouellette *et al*. [12] used probe type electrodes inside a cement-based electrolyte enclosed in a saltwater bath. Both of these batteries are closer to the form chosen for the research presented here and shown in figure 2, with cement only in the electrolyte.

The intended use of the cement batteries presented in this paper is for Impressed Current Cathodic Protection (ICCP) of steel reinforcement in concrete structures. ICCP is a method of protecting reinforcing steel in concrete from corrosion by connecting it to an inert, less noble, metal than steel and passes a low level of current through it using an external power source [13]. The recommended design current density is 20mA per m^2 of bar surface area [14] although many studies indicate that lower values are adequate [15-19]. Cathodic prevention, which is the provision of protective current before any corrosion has taken place, requires a lower current density of 2-5mA/m^2 [20]. Therefore, the testing regime incorporated a resistor load and focused on enhancing current output.

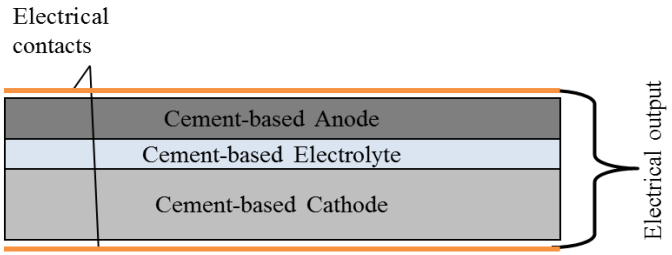

Figure 1. Layered style cement battery.

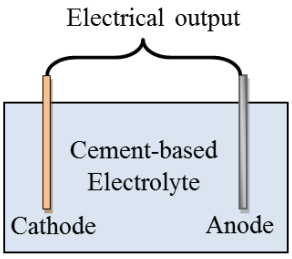

Figure 2. Probe style cement battery.

2. Battery design

2.1. Mix design

A standard form of battery was chosen (figure 2) and used to compare different electrolyte designs. The battery consisted of cement and water paste to form the electrolyte, a copper plate cathode and an aluminium plate anode. The effect of the water/cement ratio, additives and electrode spacing on current, voltage and lifespan were examined. Table 1 shows that optimal output could be achieved by designing high w/c ratios, the addition of carbon black, and adding salt for high current and lifespan. Further details of the design mixes, testing regime and outcomes are described by Holmes *et al*. [8].

Table 1. Summary of the impact of electrolyte constituents in refining the battery design.

Addition	Current (under 10Ω load)	Voltage (open circuit)	Lifespan
Increased w/c ratio	↑	=	=
Sand	=	=	=
Clay aggregate	=	=	=
Carbon black & plasticiser	↑	↑	↑
Increased electrode material	↑	=	=
Salt solution	↑	=	↑
Salt crystals	↑	=	↑
Waterglass	=	=	=
Closer electrodes	=	=	=

A final electrolyte design shown in table 2 produced an average continuous current output of 0.02mA for more than a month through a 10Ω resistor load and formed the battery design used for further development through sealing and connection in parallel as presented in this paper.

Table 2. Electrolyte constituent descriptions and proportions by weight.

Constituent	Proportion by weight (g per kg of total mix)	Description
Water	290.58	Mains supply tap water
Cement	594.94	CEM 1 (BS EN 197-1, 2000 [21])
AlKO8S2.12H2O (Alum salt)	47.28	>99% purity
MgSO4.7H2O (Epsom salt)	47.28	>99% purity
Carbon Black	9.85	Average size 30nm
Plasticiser	9.85	Sika VistoCrete 30HE

2.2. Battery cell preparation

The dry electrolyte materials shown in table 2 were weighed and passed through a 200μm sieve to remove any non-conforming lumps before being mixed with water and plasticiser and placed into 70 x 70 x 40mm plastic moulds to create the electrolyte. The electrode plates (60 x 30 x 0.5mm) were sanded and washed in a borax solution to remove any impurities or oxide layers and inserted into the wet electrolyte block protruding 5mm from the surface to facilitate connection to the resistor circuit. The batteries were then placed on a vibration table for 30 seconds to remove any remaining air. Two large blocks measuring 140 x 180 x 95mm were cast alongside using the same constituents to facilitate moisture and temperature testing over time.

In total, eight batteries and two large blocks were made as shown in figure 3. A k-type thermocouple was cast into the middle of each of the large blocks and two of the battery cells and allowed to cure under a polythene sheet for 24 hours. Four of the batteries and one of the blocks were then sealed using an acrylic based varnish suitable for cement surfaces, which was water and vapour proof. The remaining four batteries and single large block were unsealed.

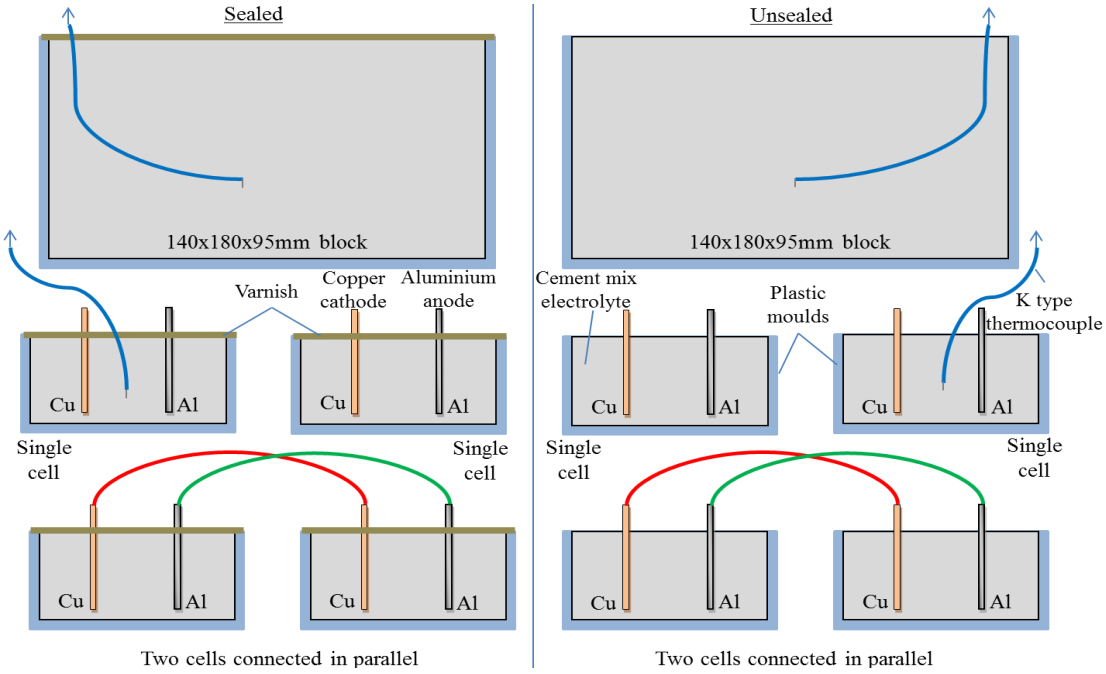

Figure 3. Schematic of sealed and unsealed batteries and blocks.

3. Recording

3.1. Resistor-loaded current

A 10Ω resistor was connected between the anode and cathode of each battery to act as a resistor load as per figure 4. Two unsealed and two sealed batteries were connected as such. The remaining four cells were joined in parallel as shown in figure 3 and connected to the resister as shown in figure 5.

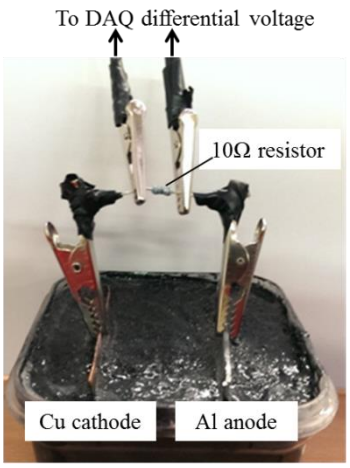

Figure 4. Differential voltage across a resistor for a single cell.

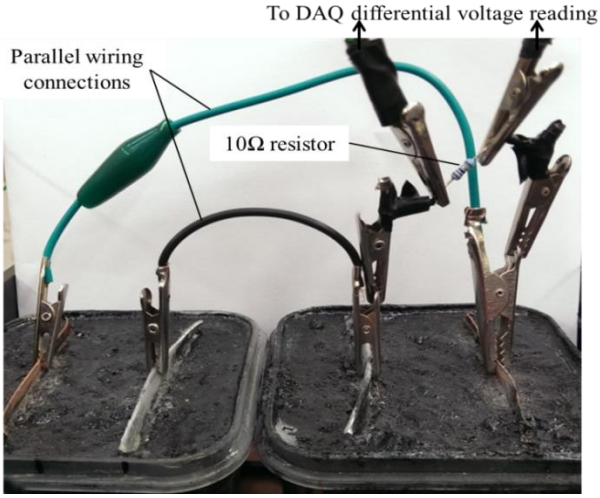

Figure 5. Differential voltage reading across a resistor for parallel cells.

A National Instruments differential data acquisition (DAQ) unit NI 9205 was used to record voltage across the resistors as shown in figures 4-6. Readings were taken every 10 seconds for the first two hours and every 10 minutes after that using a designed LabVIEW program. Current through the resistor was then obtained by dividing the voltage across it by the resistor value (10Ω). Temperature readings from the four thermocouples were recorded similarly using a NI 9211 DAQ unit. The final layout is displayed in figure 6.

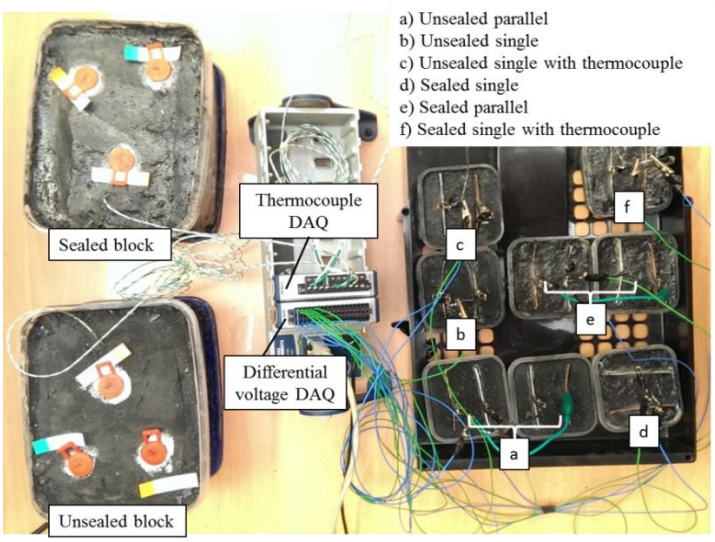

Figure 6. Setup showing DAQ for voltage recording and DAQ for thermocouple recording.

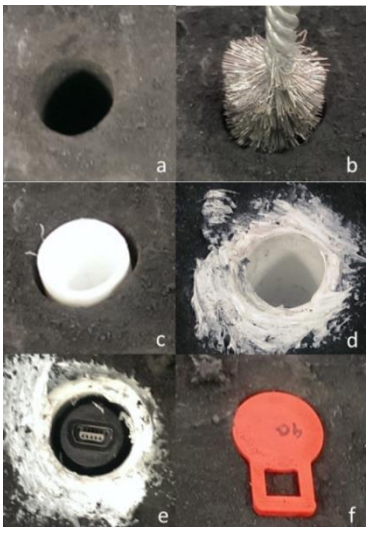

Figure 7. Steps in inserting relative humidity probes in concrete.

3.2. Internal relative humidity

Relative humidity probes were inserted into the two large blocks at depths of 40mm, 50mm and 65mm using Tramex CMEXPERT II Hygro I probes. As shown in figure 7, the holes were initially drilled into the hardened block 24 hours after casting and cleaned out. The plastic tubing provided was cut to length, inserted into the holes and sealed at the edge if required. Finally, the probe head was inserted and covered with the cap. The moisture meter could then be attached to the probe head at intervals to take recordings taken four times a day.

4. Results and discussion

4.1. Relationship with moisture

The impact of moisture retention on the discharge current of the cells was examined in two ways. Firstly, the difference in current between the sealed and unsealed cells indicates the impact of the increased moisture retention in the cells due to sealing. Secondly, the relative humidity probes that were used on the representative blocks provided an indication of the changing internal moisture condition in the sealed and unsealed cases over time.

All cells were made using the same constituents and proportions. As shown in figure 8 the sealed cells provided a resistor-loaded current that was on average 1.5 times greater than the unsealed batteries (0.066 mA unsealed and 0.101 mA sealed).

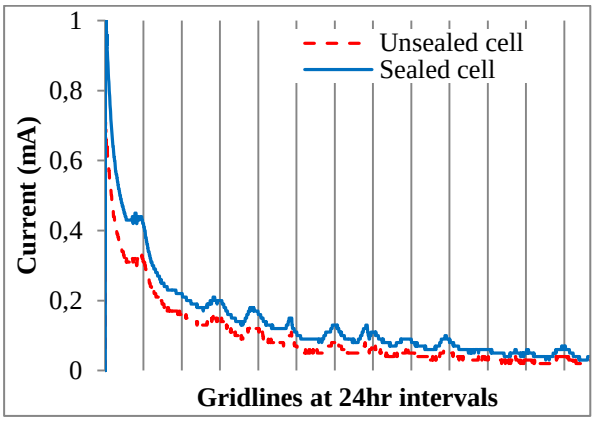

Figure 8. Discharge current through a 10Ω resistor for a sealed and unsealed battery.

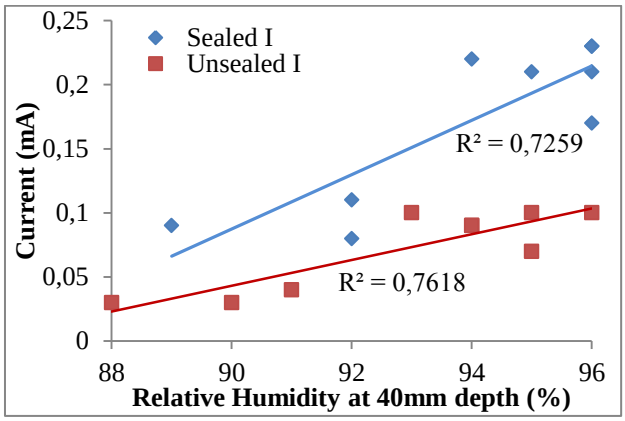

Figure 9. Relative humidity inside the blocks related to current discharged from the batteries.

Although moisture content of the cells could not be directly measured using the probe method due to size requirements, the blocks did provide an indication of the condition inside the cells. Figure 9 shows the difference between the moisture retention of the unsealed and sealed blocks. The sealed block retained on average 1% higher relative humidity than the unsealed case. The relationship between humidity and the current output from the associated cells indicates that there is a definite but not precise relationship between the two as shown by the R^2 values of around 0.7. For every 1% increase in relative humidity current was found to increase by 0.01mA for unsealed cells and 0.02mA for sealed cells. However, it is likely that during the first two weeks after casting only the area close to the surface of the large blocks will show marked differences between the sealed and unsealed cases whereas the minimum depth for probe testing was 40mm.

Over the lifespan of the battery the cells dry out as reflected by the relative humidity of the blocks. Also during this time reactants that cause the chemical reactions which create the current will be depleted and reaction products will build up on the electrodes. It is difficult to attribute the drop in current over time exactly. Further to the recorded change in relative humidity of the blocks over time, the sealed cells all showed higher current outputs than the air-dried cells consistently during the measurement period. Again this is due to both the enhanced moisture retention and the retention of reaction gases.

4.2. Relationship with temperature

The curing process naturally creates an increase in temperature as reactions take place. However, even after the peak of current during initial discharge (figure 8), small cyclical temperature variations with the environment showed a correlation with the current output. Internal temperature of the cells fluctuated cyclically with daily environmental conditions as shown in figure 10. It was observed that for every 1°C increase in temperature, the current output increased by 0.015 mA for unsealed cells and 0.028 mA for sealed cells, both with a high level of correlation with a 0.99 R^2 value. In batteries,

higher temperatures are known to correlate with greater outputs as it is favourable for chemical reactions and improves electron or ion mobility reducing the cell's internal impedance [22].

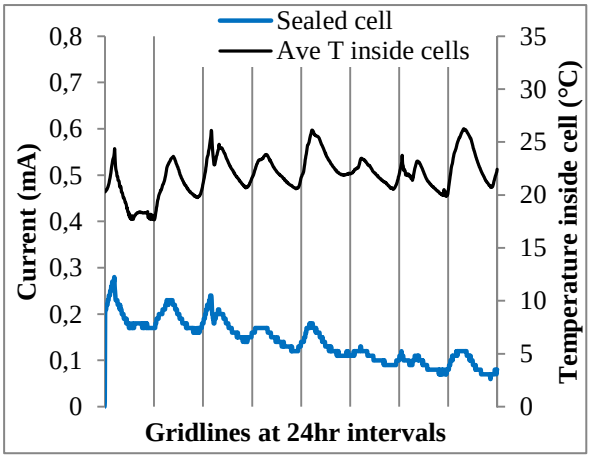

Figure 10. The relationship between temperature fluctuations within the cement electrolyte and resistor-loaded discharge current from the cells.

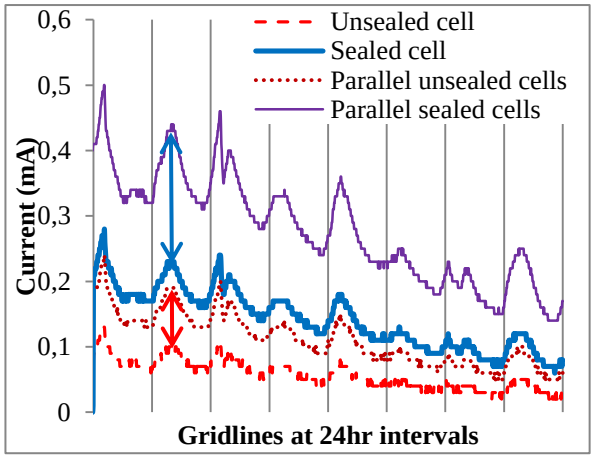

Figure 11. The resistor-loaded discharge current from single cells and two parallel-connected cells for the sealed and unsealed cases.

4.3. Connecting cells in parallel

As shown in figure 11, connecting two cells in parallel increased current output by 250% for unsealed cells to 0.16mA and 360% for sealed cells to 0.35mA. Parallel configurations are used to double the capacity while maintaining the same voltage. Capacity is the product of current multiplied by the number of hours it flows. In this case it can, therefore, be assumed that the additional current output is in sacrifice of some of the additional lifespan the cells could have otherwise expected had the current output only doubled.

5. Conclusions

This paper followed on from previous research into refining the design of a cement based battery [8] by advancing the understanding of the relationship between power output and conditions inside the cell. Impressed current cathodic protection limits the corrosion of a metal surface but requires an external direct current (DC) source. For reinforcement in steel the recommended design current density is 20mA/m^2 [14]. The cement batteries presented in this paper were designed for the intention of use in cathodic protection systems and the discharge current through a 10Ω resistor was measured. Unsealed, air-dried cement batteries were able to achieve an average of 0.066mA current over the two week recording period. Sealing the batteries with weatherproof varnish increased this value to 0.101mA. Connecting sealed cells in parallel to increase capacity further increased the current output by 360%. Although the current value (0.35mA) is considerably lower than the required 20mA for a m^2 of reinforcement surface area, it is much closer to the 2-5mA/m^2 required for cathodic prevention. Additionally, the resistivity of mild steel (15x10^{-8}Ωm) reinforcement is considerably lower than the resistor used for these experiments (10Ω), therefore, future tests should use a resistor which is more representative of mild steel.

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