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An overview of the development of cement based batteries for the cathodic protection of embedded steel in concrete

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ABSTRACT: This paper presents an overview of the cement-based batteries developed in DIT for use in the cathodic protection of embedded steel in reinforced concrete undergoing chloride-induced corrosion.

Cathodic protection delivers an external current (approximately 20mA per m² of embedded steel) which effectively polarises the internal current generated during corrosion. The batteries developed in DIT comprise of a cement-based electrolyte containing different additives including sand, aggregate, salts, carbon black and plasticiser with protruding anode and cathode metal plates. These batteries produced an initial electrical output of 1.5V and 23mA through a 10Ω resistor as measured using data acquisition units and a custom-built LabVIEW program. By enhancing the ionic conductivity and maintaining the internal moisture content in the cement pores, the batteries power and life span can be improved.

Following a concrete ponding regime to initiate corrosion of embedded steel in a concrete block sample, the power required to protect the reinforcement and arrest corrosion current was determined using a DC desktop supply. With the intention of replacing the desktop supply with a battery module ongoing work is focussing on increasing the life span of individual battery modules, improving their recharging capabilities and optimising for different shapes.

KEY WORDS: Cement-based batteries; cathodic protection; corrosion; electrolyte.

1 INTRODUCTION

The advancement of battery technology is one area that can reduce the reliance on fossil fuels. Current research is focusing on improving the lifespan, power storage and recharge capacity. The most efficient way of achieving all of these is by modifying the battery materials, specifically the electrolyte which is an ionic conductor [1]. Liquid electrolytes are preferred due to higher ion mobility and interface continuity between it and the electrodes. Solid electrolytes have lower ionic conductivities but are less likely to leak.

This paper presents a summary of the work undertaken at DIT into the utilisation of cement as a novel battery electrolyte. Results from a number of parametric studies to yield the optimum electrical current and longevity while establishing the relationships between the internal temperature and humidity with the electrical output shown. Application of the findings to protect embedded steel in concrete subject to corrosion using impressed current cathodic protection (ICCP) and a low-level external current are presented [2].

2 BACKGROUND

In any battery, ions and electrons move through the electrolyte and the circuit from the anode to the cathode respectively (Figure 1). Typical alkaline batteries use zinc as the anode, manganese dioxide as the cathode and a salt solution as the electrolyte. The electrolyte's ionic conductivity should be high with a low electrical resistance thereby allowing it to carry high current. Liquid electrolytes

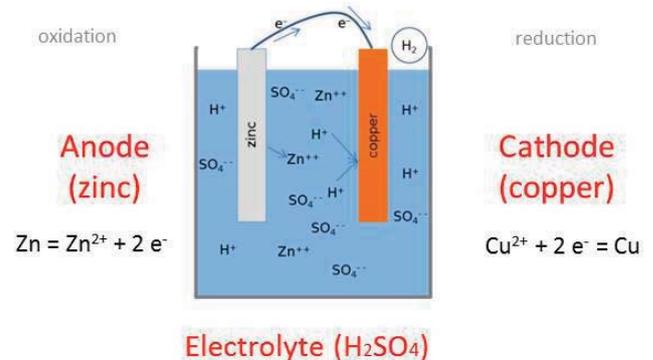


Figure 1. Conventional battery arrangement.

traditionally perform better due to the high mobility of ions. Doping solid electrolytes often improves ion movement.

The process of steel corrosion in concrete is an example of ionic flow through hardened concrete. Iron atoms removed from the steel surface by electrochemical reaction dissolve into the surrounding electrolyte solution. In concrete, this can only occur where pores exist at the steel anodic site. Electrons must therefore transfer from this anodic site to a cathodic area, which develops a surplus. The transfer of electrons occurs along the metal and creates a current between areas of differing potential (Figure 2). The ions from the reactions, such as the ferrous ion (Fe²⁺), pass into the solution trapped in the concrete pores and meet with hydroxyl ions (OH⁻) to form ferric hydroxide which reacts to form rust [3,4].

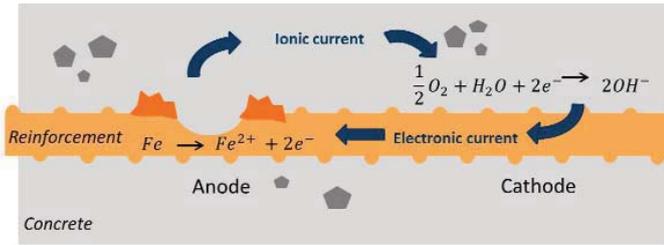


Figure 2. Corrosion process of steel in concrete [3,4].

3 LITERATURE REVIEW

Meng et al. [1] provided the initial proof of the concept that cement based batteries could provide an electrical output. Their design consisted of electrode cement layers with active additives separated by a basic cement electrolyte (Figure 3). The cathode layer was a mix of manganese dioxide particles and cement. The electrolyte consisted of cement and the anode contained cement and zinc particles. The advantage of this design over protruding electrode (non-cement-based) probes is the active phase in both anode (zinc) and cathode (manganese dioxide) are in direct contact with the electrolyte (pore solution in the cement paste) in the anodic and cathodic layers and not just at the interface with the electrolyte. The output from this type of battery design were very low with maximum open circuit voltages and currents of 0.72V and 120 μ A (current density 3.8 μ A/cm²) respectively. It also only produced current when saturated.

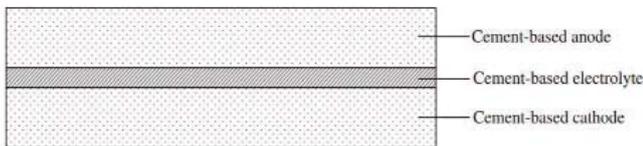


Figure 3. Layered cement-based battery [1]

Rampradheep et al. [5] used similar constituents in another layered design and produced maximum voltage of 0.6V. The current was undisclosed. Cement-batteries cast with carbon fibers and carbon nanotubes in the electrolyte layers [6] yielded maximum power outputs of 0.7V and 35.21 μ A/cm².

Ouellette & Todd [7] produced a battery incorporating a cement electrolyte between magnesium and carbon probes immersed in seawater as a corrosion-based energy harvester. Adding cement passively limited the amount of consumable oxygen rather than as a functioning electrolyte system. Attempts were made to use the battery to harvest the energy produced during corrosion and use it to power corrosion sensors [7,8]. Burstein et al. [9] developed a battery with a small current density, a steel cathode and an aluminum anode protruding from a concrete electrolyte.

The recommended design current density for (ICCP) is 20mA per m² of bar surface area [10] although many studies indicate that lower values are adequate [10-14]. Cathodic prevention, which is the provision of protective current before

any corrosion has taken place, requires a lower current density of 2-5mA/m² [14].

The following section presents the experimental work undertaken to determine the optimum cement-based battery to power cathodic protection in concrete taking into account environmental influences such as temperature and humidity.

4 EXPERIMENTAL WORK

Figure 4 shows the standard form of battery developed with different electrolyte and electrode combinations while limiting other characteristics such as size and shape. The size of the cell is irrelevant to its voltage, but does affect its internal resistance. However, it does affect the maximum current a cell can provide [3] as, with greater electrode/electrolyte contact area, there is less internal resistance and higher currents. Therefore, all batteries designed for comparison (except for the electrode ratio examinations) were of the same dimensions.

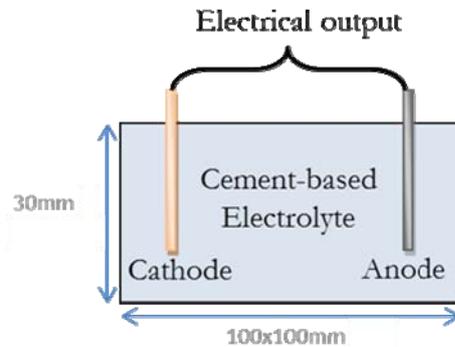


Figure 4. Basic schematic of the batteries developed

Using the highest purity non-toxic materials allowed their specific impact to be distinguished. Weighting and passing the electrolyte materials through a 200 μ m sieve removed any non-conforming lumps or bulk and achieved the desired powder format. The dry constituents were mixed well with deionised water and placed into 90 x 90 x 40mm plastic moulds (300 x 120 x 50mm were used for electrode ratio comparison tests) to create the electrolyte block. Sanding the electrode plates (60 x 30 x 0.5mm) and washing in a borax solution removed any impurities before inserting into the wet electrolyte. Each plate protruded by 5mm to facilitate the connection the resistor circuit. The fresh batteries were each placed on a vibration table for 30 seconds to remove any remaining air and allowed to set for 24 hours under a polythene sheet after which testing began.

The batteries consisted of cement and water paste to form the electrolyte, a copper plate cathode and an aluminium plate anode. The effect of different water/cement ratios, additives and electrode spacing on current, voltage and lifespan are shown in Table 1. As may be seen, the optimal electrical output and lifespans were obtained by using electrolytes with high w/c ratios, adding carbon black and salt [4].

Using these findings, an electrolyte was cast using the constituents shown in Table 2. This mix produced an average continuous current output of 0.02mA for more than a month through a 10Ω resistor load [3].

Table 1 Electrolyte constituents refining battery design.

Additive	Current (under 10Ω load)	Voltage (open circuit)	Lifespan
w/c ratio	↑	=	=
Sand & Aggregate	=	=	=
Silica fume	↑	=	↑
Carbon black	↑	↑	↑
Electrode volume	↑	=	=
Salt solution/crystals	↑	=	↑
Water-glass	=	=	=
Electrode spacing	=	=	=
Magnesium anode	↑	↑	↑

Table 2 Electrolyte constituents [3]

Constituent	Weight (g)	Description
Water	291	Mains supply tap water
Cement	595	CEM I (BS EN 197-1)
Alum Salt	47.3	>99% purity
Epson Salt	47.3	>99% purity
Carbon black	9.9	Average size 30nm
Plasticiser	9.9	Sika VistoCrete 30HE

4.1 Measurements

Measurement of current discharge was through a 10Ω resistor using a National Instruments differential data acquisition unit (DAQ) NI 9205, as shown in Figure 5. Pilot testing using a multi-meter refined the frequency of readings and likely ranges of measured current and voltages. A suitable LabVIEW programme was calibrated using a DC power unit and voltmeter with logged files written into CSV (comma separated values) format and imported directly into MS Excel after testing was complete.

4.2 Influence of temperature and internal moisture

A k-type thermocouple was cast into the middle of ten batteries to investigate the effect of internal temperature and moisture. Five batteries were sealed using an acrylic based water and vapour proof varnish suitable for cement surfaces. The remaining five batteries were unsealed. Temperature readings were recorded using a NI 9211 DAQ unit (Figure 6).

Relative humidity probes were inserted into large blocks made of the same electrolyte mix (Figure 6) at depths of 40mm, 50mm and 65mm using Tramex CMEXPERT II Hygro I probes. The holes were drilled 24 hours after casting and cleaned and the moisture readings taken.

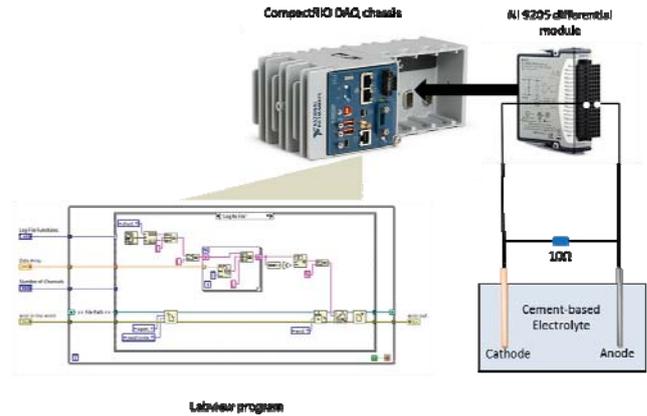


Figure 5. LabVIEW programme and DAQ used

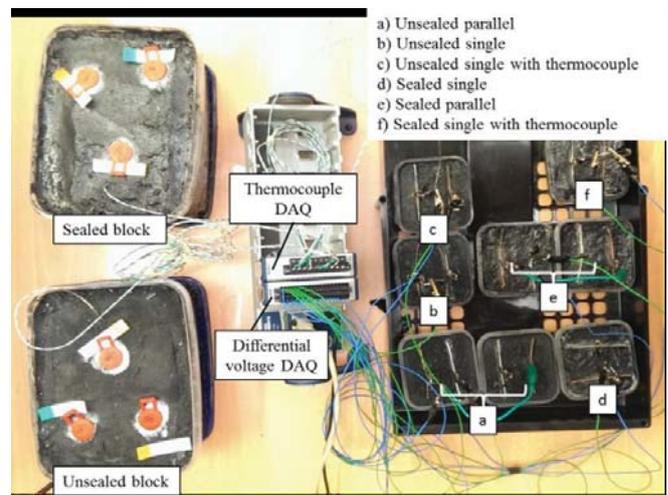


Figure 6. DAQ setup thermocouple recording.

4.3 Connecting batteries in parallel

A 10Ω resistor was connected between the anode and cathode to act as a resistor load as shown in Figure 7a. The batteries were also connected in parallel and the resistor as shown in Figure 7b.

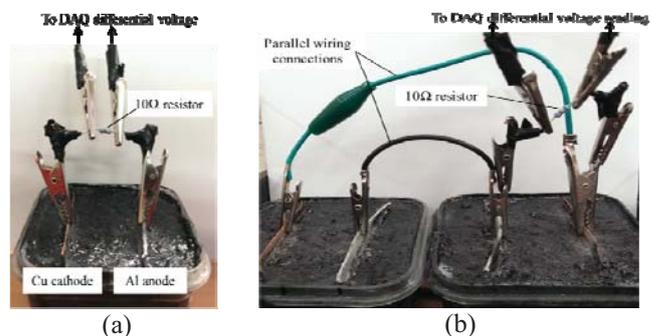


Figure 7. Differential voltage across a resistor for (a) a single cell and (b) multiple cells in parallel

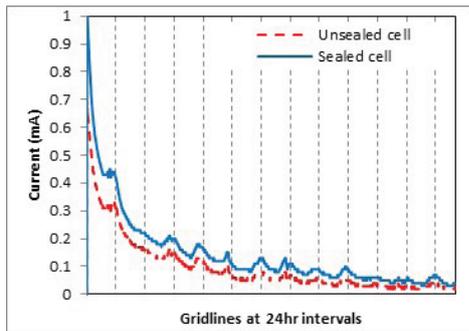
5 EXPERIMENTAL RESULTS

5.1 Effect of internal temperature and humidity

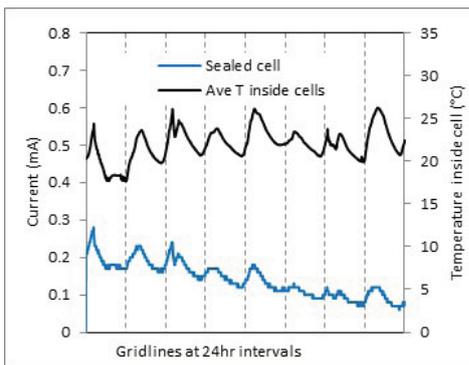
The difference in current between the sealed and unsealed cells (Figure 8a) indicates that the former performs better in terms of electrical power output.

The sealed cells provided an improved resistor-loaded current (0.101mA) compared to the unsealed batteries (0.066 mA). The sealed block retained, on average, 1% higher relative humidity than the unsealed. For every 1% increase in relative humidity, the current increased by 0.01mA and 0.02mA for the unsealed and sealed cells respectively. Over time as the cells dry, the chemical reactions that create these currents will decrease and reaction products will build up on the electrodes.

Observed temperature fluctuations found that for every 1°C increase, the current increased by 0.015mA and 0.028mA for unsealed and sealed cells respectively (Figure 8b). Higher temperatures in batteries correlates with greater outputs as it enhances chemical reactions and improves electron / ion mobility thereby reducing the cell's internal impedance.



(a)



(b)

Figure 8. (a) Discharge current through a 10Ω resistor for a sealed and unsealed battery and (b) the relationship between temperature fluctuations within the cement electrolyte and resistor-loaded discharge current from the cells

5.2 Connecting cells in parallel

Connecting two cells in parallel increased the current output by 250% (to 0.16mA) and 360% (0.35mA) for the unsealed and sealed cells respectively (Figure 9). Parallel connections

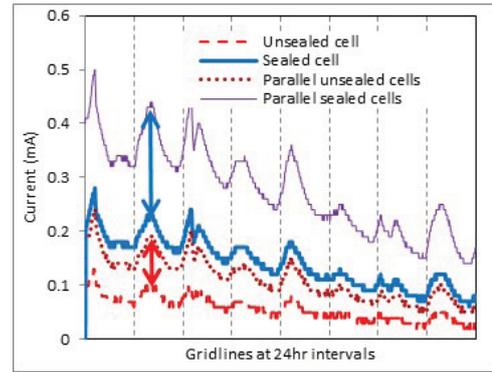


Figure 9. The resistor-loaded discharge current from single cells and two parallel-connected cells for the sealed and unsealed cases.

are commonly used to double the capacity while maintaining the same voltage.

5.3 Potential power source for cathodic protection

The amount of electrical power needed from the batteries developed above to power cathodic protection of reinforcement was determined using a measured macrocell electrochemical corrosion current. A reinforced concrete slab (245x245x110mm deep) was ponded with a 0.55M NaCl solution within a 10mm dyke in the laboratory. The top and bottom mild, and stainless steel bars respectively, were connected externally using a 10Ω resistor (Figure 10). An average corrosion current of 0.14mA was measured and peaked at 0.2mA.

A typical impressed current cathodic protection setup employed a titanium mesh anode coated in mixed-metal-oxide and cast into the ponding dyke with a cement/water mix.

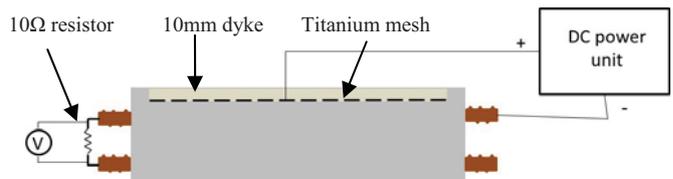


Figure 10. Experimental setup to measure the corrosion current

Figure 10 presents the results from the application of CP. As shown, there is a drop in macrocell current after application of CP. It was found that applying 0.2mA for 12 days reduced the corrosion current to zero indicating that corrosion had been arrested. Work is underway in DIT to attach a number of cement-based barriers in parallel to determine if they can mimic the results shown in Figure 11.

6 CONCLUSIONS

The results above demonstrate the potential for cement-based batteries to be used for the cathodic protection of embedded steel in concrete undergoing corrosion.

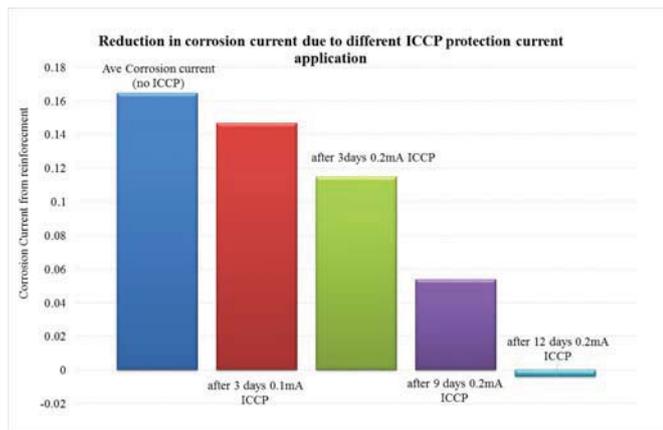


Figure 10. Change in macrocell current over time with CP application

The power output from the batteries have shown to be sufficient for CP albeit for a limited amount of time. Research is underway to further improve the ionic conductivity and maintaining the internal moisture. Work is also underway to recharge the batteries using photovoltaics thereby increasing the lifespan. Finally, research is planned for the assemblage of multiple batteries that when connected in parallel, will produce longer life spans with higher currents that are rechargeable using photovoltaics.

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