REVIEWS

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A comprehensive review on cement-based batteries and their performance parameters



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Abstract

Cement-based battery is a new area of research that is gaining popularity with the evolving idea of developing multifunctional and smart building solutions. This is deemed as a concept stirring revolution, because of the ability of the buildings to store energy and then power certain electronic applications. The core principle behind the development of cement-based batteries is the characteristics of the cement electrolyte acting as ionic conductor thereby facilitating the migration of ions between the electrodes. This review paper presents a compilation of works carried out by various researchers working towards the development of cement-based batteries along with a review on the various performance assessment parameters used by the authors, related to cement-based battery systems. In addition to the earlier works, the scope for future works in the development of cement-based batteries and the current work in progress from the authors' front are reported as well.

Keywords: Cement battery, Cement electrolyte, Ionic conduction, Multi-functional building materials

Introduction

Historically, batteries were first devised and developed in the eighteenth century by Alessandro Volta, an Italian physicist who used a stack of copper and zinc within a salt solution [1]. Since then, advances have been made in creating batteries with different electrode combinations for specific uses. Structurally, two metals or compounds of varying chemical potentials separated from each other by a separator constitute a battery. A separator should be a good electrical insulator and ionic conductor as it should prevent direct contact between the electrodes but at the same time, it should facilitate the movement of ions [2]. Irrespective of the type of battery, the basic principle and working are same across types. During discharge, chemical reaction occurring inside the battery produces additional electrons at anode and it is transferred to the cathode so that an equilibrium is maintained in the system. The metal or the compound which donates electrons is the anode and the one which accepts electrons is the cathode. The flow of electrons from anode to cathode through an external load or connection is what powers



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the devices. This movement of electrons is initiated when the electrochemical reaction starts when the battery is connected to the circuit [3].

Future building materials are now visioned in a way to offer multifunctional features like in self-sensing, self-powering and structural health monitoring. Utilization of such multifunctional materials that offers structural function (strength and stability) and nonstructural functions (sensing, heating, actuation, self-healing, electromagnetic shielding, corrosion protection, etc.) aids in cost reduction and enhanced durability and repair ability [4, 5]. Conduction concrete is one such aspect which offers a wide range of applications like cathodic protection of reinforcement bars [6], de-icing of road pavements [7, 8] and lightning protection while offering its designated structural performance. It is to be noted that unlike most of the other polymers and composites, cement matrix possesses electrical conductivity property and is not a complete insulator. A plain cement matrix has its electrical resistivity in the range of $10^5-10^6 \ \Omega$.cm [4]. By a scientific approach and suitable fine-tuning in the mix design and by addition of specific admixtures, the conductivity of the concrete can be enhanced to an extent which will have wide range of applications as mentioned earlier [7, 9]. To improve the electronic conductivity, the cementitious mix is added with carbon-based additives (carbon black, carbon nanotubes, carbon fibres, graphene powders) [10] and metallic materials (steel fibres, powders of iron and nickel) [11, 12]. New researches on determining sustainable options for the conductive additives are on the rise, where materials like recycled metallic wastes [11] and conductive rubber products [13] are some front runners. All these additives act as a filler material and are highly conductive [14].

Having briefly discussed about the conduction concrete, where the electronic conduction of the cement matrix was the area of focus [5-8], now for the application of cement matrix in a battery or a power source, the ionic conduction of the cement matrix needs a thorough understanding. Ionic conduction is the ability to permit migration of ions which is the main characteristic of any electrolyte in a battery irrespective of its type or state of nature. There are two classes of electrolytes, solid electrolyte and liquid electrolyte. In terms of performance, liquid electrolyte is generally reported to be better than the solid, due to the higher ion mobility it offers in relative to the solid electrolyte. Economically as well, liquid electrolyte is cheaper than the solid electrolyte. Furthermore, the contact interface between electrolyte and electrodes is more in liquid electrolytes thereby reducing the offered resistance. However, one major disadvantage associated with the liquid electrolyte is that it is prone to leakage upon disposal and even during its usage. The environmental hazard owing to the toxic leakage of such wastes is a major problem across the world currently [15]. The other class, solid electrolyte, is expensive but the issue of leakage is eliminated [16]. However, unlike in liquid electrolyte, the ionic conductivity of solid electrolyte is not adequate enough at room temperature, and therefore, it requires a bit of excitation to enhance its conducting ability. From the researches on solid-state batteries, it is evident that the spotlight is on finding the right solid electrolyte that possesses a higher ionic conductivity [17, 18]. This has in fact paved advances in the development of new combinations in lithium-ion and sodium-ion batteries. The scope of interest of this paper is the cement-based electrolyte battery, which categorically falls under the solid-state classification. This review paper is written by first introducing the working of conventional battery and then linking the cement-based battery system's advent, concept and types with the conventional, and then briefing about the performance characteristics associated with the cement-based batteries. A tabulation with past researches in cement-based batteries is compiled in this review paper.

Basics of batteries

Battery, an electro-chemical device, is a stack of voltaic cells designed to provide a higher current or voltage to an external circuit. Elementarily, it is constituted with two metal electrodes (anode and cathode) that are immersed in a chemical mixture (electrolyte). In process, it harnesses electric current upon electron transfer as a result of an electrochemical reaction (oxidation and reduction) occurring inside the battery [19]. Electronically, oxidation is loss of electrons and reduction is the subsequent gain of electrons. For illustration, the most common lead-acid battery which has application in automobiles shall be considered. In lead-acid battery, one electrode is made of lead (cathode) and another electrode is made of lead dioxide PbO₂ (anode). In this case, both electrodes are metal and are electrical conductors. The electrolyte is the diluted sulphuric acid. When this cell arrangement is connected to an external circuit, the electrons have paved a path to move from one to the other and the flow of electrons constitutes an electric current [20]. This process of the battery/cell providing electrical energy to an external load or circuit is termed discharging, since it is accompanied with the depletion of internal chemical reserves (active elements in anode, cathode and electrolyte). The output voltage harnessed from any battery is dependent on the electrodes, electrolyte and the corresponding electrochemical reaction between them. Now, when this electrochemical reaction inside the cell is reversed by supplying a negative current (flowing from negative to positive), cells can be recharged and those are called secondary cells. The cells where the reversal is not feasible, those are called primary cells [21].

Cement-based batteries

Development of cement-based batteries, where the cement matrix is the electrolyte, is in the spotlight of some research groups working in the area of multi-functional building materials. The advent of this technology in a full scale would bring about a huge change in the construction sector because of the ability of large volume of concrete buildings/ structures to harness electricity on its own [22] and store without any dependence on the external sources for certain specific application. Cement-based battery is a solidstate battery in which the pore water (solution) within the hardened cement paste is the primary electrolyte medium through which ion migration would occur [23]. Hence, in the development of cement-based batteries, the main focus is on the enhancement of electrolytic (ionic) conduction property of the cement paste.

There is a requirement of power sources at remote places for certain operations like powering of structural health monitoring systems or an Impressed Current Cathodic Protection (ICCP) system as concerned to the infrastructure maintenance. Providing exclusive generators and power lines at difficult-to-access locations involves a lot of practical and economic complications and this had paved way for the development of cement-based batteries, by which certain low-power operations shall be taken care of the building itself in a self-sustainable manner. With respect to corrosion protection, there are studies which have reported that a small current density applied intermittently could arrest the corrosion occurring in steel reinforcement. Study by Glass et al. [24] reported that an intermittent current density of 6 mA/m² was able to counter the corrosion rate of approximately 60 mA/m² in reinforced concrete system. Cathodic protection and cathodic prevention are two kinds by which the steel reinforcements in concrete structure are protected from corrosion initiation and progression respectively. As far as cathodic protection is concerned, a recommended current density is around 5–20 mA/m² while for cathodic prevention a much lower current density of 1–2 mA/m² only is required [25]. Therefore, the cement-based batteries can be projected for the application of cathodic prevention, a low-power operation that could operate at 1–2 mA/m².

The fact that the cement system is rich in ionic composition and is a good ionic conductor [9] must have been the realization point for Berstein and Speckert in 2008 who made an initial attempt to utilize cement paste as an electrolyte [26]. The initial system's electrodes were made of aluminium anode and iron cathode, making it an aluminium/ water cell because the reduction of water to hydrogen at the cathode was a half-cell process. The battery system reported to have an operating voltage of 0.4 V and power output of 100nW/cm² at no oxygen atmosphere. However, aluminium immersed in cement matrix exhibited physical degradation as reported by the authors even when not under load which would eventually make the anode porous and therefore lose its integrity with time. Also, the dissipation of liberated hydrogen at cathode, as a result of reduction reaction of water, is critical since hydrogen might cause steel embrittlement and lead to crack formation. Therefore, keeping it in sight, this battery system was claimed to be applicable only for a very low power operation, such that the hydrogen liberation shall always be kept under check [26].

Forms of cement-based batteries in the development

Researchers have adopted different dimensions and styles for the cement battery development. Technically, the performance is measured in terms of voltage per area, current per area and power output per area of the battery, and therefore the size variations among batteries developed by researchers across the world should not be confusing for its performance comparison. As of date, two basic forms of cement-based batteries had been widely reported and they are (i) probe style and (ii) layered form. The classification is based on the form of electrodes being used. The anode and cathode in the probe style are typically plates or rods partially immersed inside the set cement-based electrolyte, while in the latter, a layer of cement-based electrolyte is sandwiched between layers of cementbased anode and cement-based cathode. Also in the layered form, the active electrode component is distributed in powder form or as a solid rod or even a combination of both. A schematic representation of the two forms of cement-based battery is shown in Fig. 1.

Layered batteries

The first attempt in formulating a formal mix for the development of cement-based batteries was carried out in 2010 [27] based on the limitations of previous developments of Burstein and Speckert [26]. A monolithic battery design with anode, cathode and electrolyte, all based out of cement, was the primary idea behind the authors' work and in which electrolyte was the pore solution. In comparison with the conventional batteries,



Fig. 1 Different types of cement-based battery. a Layered battery. b Probe style battery

cement-based batteries constitute a common electrolyte, which is cement matrix unlike the commercially available alkaline batteries in which the elements are all assembled and distinct. In the work of Meng and Chung, active particles of anode and cathode characteristics were dispersed within the cement paste and structured in layer wise, with the denser of the two positioned in the downside, possibly for a better mechanical stability. The authors had attempted to cast the layers in succession and cured it as one. The main constituents utilized by the authors in the research were cement, zinc powder (anode), manganese dioxide powder (cathode), and carbon black (conductive additive). The thickness of the layers were varied with the anode: cathode thickness ratio kept at 0.5. Significant performance was reported from the battery with dimension of 80 mm \times 40 mm \times 14 mm, in which the split-up of 14-mm thickness is as follows: anode—4 mm, electrolyte—2 mm and cathode—8 mm, and was discharged at $60\mu A$ (1.88 $\mu A/cm^2$) yielded a maximum output voltage of 0.72 V and lasted 3.4 h showing a capacity of 0.204mAh [27]. The 1.88 μ A/ cm^2 was significantly higher than the previously devised battery by Burstein and Speckert by 650%. One of the notable findings from the study was the fact that decreasing the discharge current increases the life span of the battery [27] but however, it is the end application that is intended which will decide on the discharge current.

With same constituents as of Meng and Chung [27], Rampradheep et al. included self-curing agent (poly ethylene glycol) and constructed a battery of size 100 mm \times 50 mm \times 18 mm, in which the 18-mm thickness is composed of 5-mm anode, 3-mm electrolyte and 10-mm cathode. Output voltage of 0.6 V was reported in the study [28]. Qiao et al., in their research, also used manganese dioxide powder and zinc particles in the cathode and anode layers along with the cement matrix. In addition to the carbon black as conductive additive, carbon fibres and carbon nanotubes found a place in the mix of each layer [29]. Geometrically, a cylindrical battery of 30-mm diameter with 10 mm of anode layer,10 mm of electrolyte layer and 50 mm of cathode layer was the basic design in the study adopted by the authors. Performance-wise, minimum of 0.7 V and 250µA was reported in a 24-h period with a peak voltage of 1.4 V which occurred during the early period of the cycle. As a part of the work, the authors also attempted to charge a supercapacitor using an ultra-low power booster converter and maximum voltage achieved was 2.34 V after 32 h of charging [29].

The electro-chemical reactions behind the outputs of all the layered batteries involving the manganese dioxide and zinc particles as the active components in cathode and anode layer respectively are given below:

In the anode layer :
$$Zn + 2OH \rightarrow ZnO + H_2O + 2e^{-1}$$

The anodic reaction is an oxidation reaction which results in the release of electrons. The free electrons will move through the electrolyte layer and reach cathode and results in a reduction of manganese dioxide dispersed in the cathode layer.

In the cathode layer : $2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$

In 2015, Holmes et al. made attempts to devise three styles of battery, namely layered, can style and probe style. In layered, similar to the previous works discussed, manganese dioxide particles and zinc particles in the cathode and anode layer respectively along with the cement base with carbon black as conductive additives in the layers except electrolyte [30] were used. Conductive copper strip on either side of the battery was used to measure the output. A 10Ω resistor was connected between the electrodes and voltage and current measurement were taken from the battery across the resistor. From the layered style battery, a very low current of 0.001 mA was reported the same also dropped to 0 mA within a short span of time [30].

Zhang and Tang in 2021, constructed a cement-based layered battery with a recharging capability, and therefore the selection of materials was in such a way that the recharging feasibility was there [31]. A highly alkaline cement electrolyte layer was achieved by the inclusion of an alkaline solution combination (KOH and LiOH.H₂O) in the study. An ion-exchange resin was used in cement electrolyte mix to serve a dual purpose of increasing the ionic conductivity and offer a high electrical resistivity for the middle layer. For improving the electrical conductivity, short carbon fibres at low volume were included in the anode and cathode layers instead of the carbon black or carbon nanotubes as used in the previous studies. A good mechanical toughness and reduction in drying shrinkage are supplementary advantages that carbon fibres offer to the cementbased electrode layers. As far as electrodes are concerned, nickel hydroxide powder and iron powder were used as the active component in the cement-based layers [31]. The optimization of short carbon fibre content and the type of dispenser was carried out by preparing a conductive mortar and testing its resistivity. It is the combination of good workability and less resistivity that aided in the finalization of the mix for the cement electrode layer. With no satisfactory output current in their initial work which cannot be used for commercial purpose, a different approach was made by the authors in which the active components (powders) were electroplated to a carbon fibre mesh, which was then laid within the corresponding cement-based electrode layers. Carbon fibre meshes electroplated with nickel powder and iron powder for cathode and anode, and this combination exhibited better performance in terms of current output which was greater than 2 mA for 22 h with an electrical capacity of 88mAh. The battery in six charge-discharge cycles exhibited an average energy density of 7Wh/m² [31]. As far as layered battery construction was concerned, a common issue faced and reported by the associated

people was the workability and crumbling nature of the set layers [27] when overlaying. The overall compilation of the various system devised by the researchers is tabulated in Table 1, along with the details of the probe-style batteries for a quick understanding. A timeline depicting the cement-based battery development over the years by various researchers is shown in Fig. 2.

Can style and probe style

For the can-style battery design, Holmes et al. [30] used an aluminium can which served a dual purpose of acting as an anode and as the mould for the battery. The cathode was the copper plate and it was safely insulated from the anode aluminium can to prevent short circuit. Cement mix as electrolyte was filled in the can, with inclusion of various constituents and additives. Similar to earlier works, addition of carbon black again showed improvements in the output. Also, increasing the cathode ratio of the can battery (size of copper plate) enhanced the current and voltage output. Output-wise, the resistor-loaded current was observed to dip suddenly from 19 mA to less than 5 mA [30] which eventually dropped further with further ageing.

Many studies were conducted on the probe-style battery only. As discussed in the earlier section, the structure of the probe-style battery is made of two electrodes in the form of metal plates kept in a common cement-based electrolyte. In addition to the carbon additives added to the cement mix in layered battery design by various researchers, Holmes et al. in their work had recommended the use of inorganic salts, particularly in solid form rather than solution for better performance in current output and lifetime [30]. Also, a better output has been reported in the work when the choice of anode was magnesium instead of aluminium.

However, more studies with several alterations and inclusions in the system by the authors were conducted in their subsequent research programmes, where copper and aluminium electrode combination were adopted. Geometrically, cement electrolyte in the mould size of $70 \times 70 \times 40$ mm and with the protruding electrode plates of $60 \times 30 \times 0.5$ mm had been used to conduct the electrical performance tests [33]. In addition to the electrical measurements, the authors also tested blocks of battery electrolyte for the effect of temperature and humidity on the electrical performance. In view of imparting additional mechanical strength to the battery, the authors incorporated sand and light-weight clay aggregate, which however did not affect the electrical output of the battery system. Temperature influenced the battery output, as an increase of 0.03 mA current for every increase of 1 °C considering the sealed cells and in the unsealed cells, the increment of 0.015 mA for unit rise in temperature was reported [33]. With parallel connection of multiple batteries, maximum output of 0.35 mA [34] was also reported. The basic battery science of parallel connection is that it yields added capacities and current while series connection yields added voltage and the same had been applied here.

A detailed parametric study with an aim to further optimize the cement battery system was conducted by Byrne et al. [34]. The output electrical measurement of voltage and resistor-loaded current along with the lifespan of the battery were the measure of performance in the experimental plan. The authors had made a systematic approach in studying the effect of various parameters included in the making of battery and optimized each constituent at every level of the experimental program. A list of parameters

Author and year	Specimen type and dimensions	Electrode configuration	Electrical parameters reported	Max output
G T Burstein and E.I.P Speckert 2008 [26]		Anode: aluminium Cathode: reduction of water to Hydro- gen on steel	 Operating voltage (V_{op}) Power output (watt/cm²) 	$V_{op} = 0.4 V$ Power out- put = 100nW/cm ²
Meng and Chung 2010 [27]	Type—layered Dimen- sions—80 mm × 40 mm (Plan)	Anode: zinc parti- cles dispersed in cement matrix Cathode: man- ganese di oxide particles dispersed in cement matrix	 Open circuit voltage (V_{oc}) Power output (watt/cm²) Capacity (mAh) 	$V_{oc} = 0.72 V$ Power Out- put = 1.4 μ W/cm ² Capacity = 0.2mAh
Rampradheep et al. 2012 [28]	Type—layered Dimen- sions—70 mm × 20 mm (Plan)	Anode: zinc particles Cathode: man- ganese dioxide particles Self-curing agent to retain moisture within the battery	• Open circuit volt- age (V _{oc})	$V_{oc} = 0.6 V$
Qiao et al. 2014 [29]	Type—layered Dimensions—30 mm dia (cylindrical geometry)	Anode: zinc particles Cathode: man- ganese dioxide particles	• Voltage (V) • Current density (I _d)	V > 0.7 V $I_d = 35.21 \mu A/cm^2$
Holmes et al. 2015 [30]	Type—layered Dimen- sions—150 × 150 mm (plan)	Anode: zinc particles Cathode: man- ganese di oxide particles (with carbon black inclusion)	 Open circuit voltage (V_{oc}) Resistor-loaded current (I_{RLC}) 	V _{oc} =0.74 V I _{RLC} =0.001 mA
	Type—can style Dimensions—66 (dia) × 100 mm (plan)	Anode: aluminium can Cathode: copper plate		I _{RLC} =4.8 mA
	Type—probe style Dimen- sions—100 × 100 mm (plan)	Anode: magne- sium/zinc/alu- minium Cathode: copper		(V _{oc}) = 1.34 V (Mg) 0.79 V (Zn) 0.52 V (Al)
Holmes et al. 2016 [32]	Type—probe style Dimensions—electrolyte $(70 \times 70 \times 40 \text{ mm})$ Electrode $(60 \times 30 \times 0.5 \text{ mm})$	Anode: aluminium Cathode: copper	 Open circuit voltage (V_{oc}) Resistor-loaded current (I_{RLC}) Life span 	I _{RLC} =0.101 mA
Byrne et al. 2016 [33]	Type—probe style Dimensions—electrolyte $(90 \times 90 \times 40 \text{ mm})$ Electrode $(60 \times 30 \times 0.5 \text{ mm})$	Anode: aluminium Cathode: copper	• Open circuit volt- age (V _{oc}) • Resistor Loaded Current (I _{RLC})	$V_{oc} = 1.5 V$ $I_{RLC} = 0.35 mA (2)$ batteries in parallel connection)
Byrne et al. 2017 [34]	Type—probe style Dimensions—electrolyte $(70 \times 70 \times 40 \text{ mm})$ Electrode $(60 \times 30 \times 0.5 \text{ mm})$	Anode: magne- sium, Cathode: copper	 Open circuit voltage (V_{oc}) Resistor-loaded current (I_{RLC}) and corresponding voltage (V) Life span 	I _{RLC} = 0.59 mA (quas steady) Life span = 238 h

Table 1	Compilation	of research work	s related to ce	ment-based batteries

Author and year	Specimen type and dimensions	Electrode configuration	Electrical parameters reported	Max output
Zhang and Tang 2021 [31]	Type—layered Dimen- sions—90 × 90 mm	Anode: iron powder Cathode: nickel hydroxide powder (electroplated to carbon fibre meshes)	• Open circuit volt- age (V _{oc}) • Resistor Loaded Current (I _{RLC}) • Capacity (mAh) • Energy density (Wh/m ²)	$V_{oc} = 1.8 V$ Capacity = 62mAh Energy density = 7 Wh/m ²
			D	





optimized in the study is as follows: (i) water-cement ratio, (ii) aggregates, (iii) carbon additives, (iv) salts (in solid form and as solution), (v) sodium silicate, (vi) electrode combinations, (vii) anode–cathode ratio, and (viii) electrode spacing. In addition to the previous works carried out in the area, the authors included the use of sodium silicate solution, which has a high concentration of conductive ions.

The parameters under the spotlight in the study can be grouped under two categories: (a) electrolyte-related and (b) electrode-related. Among the parameters listed above, (i) to (iv) are electrolyte-related and (vi) to (viii) are electrode-related while (v) is common to both since the sodium silicate solution was used in electrolyte mixing and as well as for coating the electrodes. However, by any means, inclusion of sodium silicate solution reflected no significant change in the output or the battery's life span. The constituent and the corresponding effect on the electric performance of the system were reviewed and are presented in Table 2, along with the reasons pointed out based on material science and authors' experimental work and inferences from the studies.

Now, considering the electrode-related parameters in the study, the combination of magnesium and copper as anode and cathode had delivered the maximum output and enhanced life span. The finding also goes with the fact that among the choices of anode (Mg, Al, Zn), Mg is the most active metal according to the galvanic series as shown in Table 3, followed by Zn and then Al.

The overall increase of cathode and anode ratio in the system increases the current output and the life span of the battery due to the presence of more active materials that can participate in the electrochemical reaction. However, the electromotive force (emf) of the electrodes being constant for a combination (Table 3), the open circuit voltage would not fluctuate. It is a conception that the amount of electrolyte between the electrodes should be as minimum as possible so that the distance the ions need to cover to

Addition	Constituents	Effect on electric output	Remark/reason
Fine aggregate	a) Sand [30, 31] b)Light-weight clay aggre- gates [33, 34]	No impact	Unless the aggregate phase is reactive, no effect would be observed on the electric performance since it is the electrolyte's ionic conductivity that governs the batteries per- formance. However, the inclu- sion of non-reactive aggregate phase provides a mechanical stability to the battery system and prevents the formation of cracks along the electrode– electrolyte interface
Carbon addi- tives (electron conductive particles (ECP))	a) Carbon black [27, 30, 32–34] b)Activated charcoal [28]	Improved capacity and cur- rent discharge performance and no change in open circuit voltage	The carbon-based additives in any form are deemed as good electronic conductors and therefore do not effectively improve the ionic conductivity of the system. Also, the carbon powders being spongy in nature would absorb too much water, thus making the elec- trolyte mix harsh. To counter the same, some authors had incorporated a dose of super- plasticizer, which would have chemicals that have the ability to improve the ionic conduc- tivity of the pore solution. Therefore, the improvement in the electric performance upon the addition of carbon addi- tives cannot be claimed
Inorganic salts (ionic conduc- tive particles (ICP))	a) Sodium chloride [30, 34] b) Epsom salt[30, 32–34] c) Alum salt [30, 32–34] (as solid and as solution)	Improved the overall perfor- mance and in fact addition of salt in solid form enhanced the output more than when added as solution	Salts upon addition with water would readily dissociate into free ions that have all the capa- bility to effect a change in the pore solution. However, as far as alum salt is concerned, the aluminium ions would form ettringite quickly upon mixing with cement and with hydra- tion, resulting in a harsh mix. This observation though was not reported in the past works; the same was observed in the current work of the authors
Pozzolan	Silica fume [34]	Improved the current discharge performance and lifespan of the battery system	Silica fume is known to densify the microstructure of the con- crete, which means reduction in the porosity and thereafter pore solution (electrolyte). However, there is literature backing that a higher percent- age addition of silica fume would result in higher porosity [35] which could be the idea behind this addition and posi- tive effect

 Table 2
 Compilation of effect of additives in the cement-based electrolyte

migrate from one electrode to another is less and ultimately the resistance is less [27]. But however, according to the authors, no change in the voltage or current output or life span was observed with the change in spacing of electrodes. This finding implies that the

Material		Standard Electrode Potential (V)
Magnesium	0	-2.363
Aluminium	♦ nodic	-1.662
Zinc	A	-0.763
Iron		-0.440
Nickel		-0.250
Copper	dic	+0.345
Platinum	atho	+1.200
Gold	O O	+1.498

 Table 3
 Standard
 electromotive force (emf) series as measured against a hydrogen reference electrode [36]

amount of electrolyte between the electrodes does not affect the electrical performance in any means, which is in contrast to the findings of Meng and Chung [27].

Parameters of interest

Having reviewed the previously conducted experimental works in the area of cementbased battery, this section is written to focus on the different parameters and measurements that are relevant for assessing the performance of the batteries. This section is important particularly for the fact that different researchers use a different testing methodology, and the sizes of batteries were all different. The general idea is that the more the reactive component is present (electrodes), the reaction will last longer. Since the dimensions and the configurations of the battery system varies among the research groups, current and energy in terms of area of battery system or the electrode (termed as current density and energy density) is preferable to make a comparison among the works.

From the research works previously discussed, the parameters that were considered in each work and the corresponding maximum output reported are tabulated for easy comparison as in Table 1. A brief description on the parameters is given in the following subsections, which is written to introduce battery terminologies and testing methodologies from a cement-based battery perspective.

Open circuit voltage

Open circuit voltage (V_{oc}) is usually the voltage measured across the electrodes under a no-load condition [37]. It is a function of electrode type and combination, composition and the pH of the electrolyte system. The value is equivalent to the theoretical voltage. Practically it is determined by connecting a digital multimeter in DC voltage mode across the two electrodes, and the measured open circuit voltage is the potential difference between the corresponding anode and cathode. A representative image of determining the open circuit voltage (from the authors' work) is shown in Fig. 3.

Almost all researchers would have reported the open circuit voltage, and it can be evidently observed that irrespective of the enhancements in the cement mix of the system,



Fig. 3 Open circuit voltage measurement

the electrode combination strongly influences the open circuit voltage. In the paper of Holmes et al. [30], with the combination of (anode–cathode) Mg-Cu, Zn-Cu, and Al-Cu, the reported V_{oc} were 1.34 V, 0.79 V and 0.52 V respectively [30]. The trend can be accordingly observed in the emf series as well; the same is given in Table 3.

Resistor-loaded current

As stated earlier, open circuit voltage is the measurement taken in an open condition without any load while the resistor-loaded current is the current measurement taken across a resistor (load) which is connected to the battery system. So ideally when the battery is in discharge, the voltage will drop across the resistor with time and the current through the resistor is calculated using ohms law ($V = IR \rightarrow I = V/R$). This is the resistor-loaded current.

The research group based in Dublin University, Byrne and Holmes, in their work, had used a 10Ω resistor [30, 32–34] in all their works and reported the resistor-loaded current for all the specimens. Basically, the authors attempted a discharge test by connecting the known resistance across the cement-based battery and evaluated its performance. Similar to the work of Byrne and Holmes, Zhang and Tang [31] connected a 165Ω

resistance [31] across the electrodes and tested the battery's performance by evaluating the current during the discharge. Since it is a continuous measurement, the quasi-steady (almost stable) current value was reported in the papers. A representative image of the measurement strategy of resistor-loaded current from the current work carried out by the authors of this paper is shown in Fig. 4 along with a line circuit diagram.

Figure 4a and b are from the current works carried out by authors in which a switch has been included in the circuit to perform multiple discharge cycles for better assessment of battery's life and performance.

Discharge life

Batteries' life is denoted in a different way depending on the scenario, either in terms of lifetime in years or in number of charge–discharge cycles that can be successfully delivered. For a cement-based battery with the limited research and attempts, the reported discharge life is very small as compared to the conventional commercial batteries which extend to months and years.

From the literature, with respect to the cement-based batteries, max lifespan reported was 21 days recorded by a battery designed by Byrne et al. [34] delivering a current of 0.59 mA. For 1 mA, the lifespan was 4 days for the same system and so a more obvious relationship between the delivering current and lifespan can be interpreted. The more the current discharge, the life span will be reduced; therefore, a scenario dependant call is appropriate during the application of the battery system. The same has been observed in the earlier works of Meng and Chung [27], who reported that the lifetime extended when the batteries were discharged at 80 μ A while attempting three discharge currents (80 μ A, 100 μ A and 120 μ A) [27]. Generally, for a battery, its lifetime depends on factors like operating temperature, mechanical stresses, charging and discharging rate. Increase in temperature and high charging rate tend to reduce the life and durability of the battery [38].

Capacity

Capacity is a fundamental specification associated with any battery system. Capacity of a battery is usually represented as Ampere-Hour (Ah) and by definition, it is the product of current drawn from the system while it is capable of supplying the load until the voltage is dropped to lower than a stipulated value of the cell. For instance, a battery



Fig. 4 Resistor-loaded current measurement mode. a Line circuit diagram. b Representative image

with capacity of 10Ah can deliver a constant 10A current for 1 h continuously and the same battery can be made to deliver 1A for 10 h. Battery's manufacturer would specify a current value as rated current, which will be the constant discharge rate that will correspond to the standard load conditions [39].

Alternatively, capacity of battery is a direct interpretation of the amount of charge that can be delivered at a stipulated voltage and it is directly proportional to the quantum of electrode material present in the system. The other factors influencing the capacity of the battery system are density and temperature of the electrolyte and age of the battery. Technically, increased temperature and high density of the electrolyte would result in higher capacity of the battery but however the same is not practically feasible and also it reduces the battery life. With respect to age, the older batteries which had undergone number of discharge cycles will have less capacity in comparison to the new battery, which is related to the consumption of active materials present in the electrodes with successive discharge cycles.

Few researchers have reported the capacity of the cement-based batteries in their work, one is Meng and Chung [27], where the authors have reported a capacity of 0.2mAh [27] for their battery design. In the work of Zhang and Tang [31], the cement-based battery constructed using the carbon fibre meshes electroplated with active components (Ni and Fe) was reported to have a capacity of 62mAh in the first cycle, which gradually reduced to 55mAh in the 6th discharge cycle [31].

Practically, the capacity of the battery is measured as the product of quasi-steady current that the battery system is able to deliver upon discharge cycle and the discharge time, the time at which the voltage of the battery system goes below the a pre-decided stipulated value. This can be carried out using a digital Source Meter Unit (SMU), which can be used to discharge the battery at a specific current rate and with the time taken by the battery system to reach a lower cut-off voltage, the capacity shall be calculated. Sometimes power capacity is also used for rating the batteries, which is voltage multiplied by the battery capacity(Ah) and energy is usually represented in watt-hour (Wh). There are instances in the past research when the authors had reported capacity and energy with respect to the area of electrodes like Zhang and Tang [31] who reported the energy density in terms of Wh/m².

Current density

Represented in terms of Ampere per square metre (A/m²), current density denotes the amount of electric current that flows through a unit area, specifically cross-sectional area of an element. In batteries, surface area of the electrodes is considered. Batteries' performance irrespective of the size can be standardized in terms of the current density and a comparison can thus be made. The cement-based battery developed by Qiao et al. [29] is reported with a current density of 35.21μ A/cm² (250 μ A from a cylindrical battery of diameter 30 mm, and the plan area is considered).

Alternatively, some researchers also use power density to rate the batteries which is conventionally represented in terms of watt per square metre (W/m²). For instance, the earliest work in cement-based battery by Burstein and Speckert [26], the reported power output from the battery system was 0.1 μ W/cm² and Meng and Chung [27], who

followed the earlier work reported an output power of 1.4 $\mu W/cm^2$ from their layered battery system.

In regard to the cement-based batteries, the researchers have adopted the quasi-steady current value (and initial running voltage) during the discharge and the plan area of the battery system for determining the current density and the power density.

Conclusions

A review of available literatures on the past works pertaining to the development of cement-based battery systems was carried out and documented through tables in this paper. Briefing on the performance characteristics related to electrical parameters is also provided to give insights for the researchers with civil engineering or materials back-ground about the basic testing methods for a battery system. From this review, some inferences and recommendations are made and taken forward for further development of the work which are as follows:

- i. A conflicting conclusion was observed where the authors had reported the effect of spacing of electrodes on the electrical performance of the system. Byrne et al. [34] had reported no effect in the work while Meng and Chung [27] had indicated that the electrolyte between the electrodes governs the actual distance that the ions are required to travel which in turn will have a significant effect on the electrical performance of the battery system.
- ii. Though magnesium as the anode option provides a higher open circuit voltage as reported in [30], in the subsequent researches, the preference was given to aluminium which may be accounted to the reasons of pure magnesium's lack of stability in harsh conditions. For the same reasons, alloys of magnesium shall be attempted as an anode option in combination with the copper cathode.
- iii. The battery system reported by Zhang and Tang [31] with capacity of 62mAh and highest operating voltage in comparison with the other past works can be considered the best-performing cement-based battery reported so far. Characterization of the system with more appropriate I-V curves and C-ratings as reported for conventional battery system can be carried out for the same system to take it forward in commercial aspects.
- iv. However, in terms of robustness and battery being a part of the structure itself, it becomes necessary to study the strength aspect of the component and no work had reported the same.

In addition to the above points, there are more future scopes like adopting 3D printing technique for making layered batteries by which the common workability issue as reported in the literature can be counteracted. By this, the placing of layers also becomes easy with complete automation of laying the layers instead of manually placing the hard layers in its crumbling consistency. More characterization like for any other active devices like batteries, solar cells such as I-V curves and EIS plots shall be made for cement-based battery specimens also. As a matter of fact, the authors are already working in some of the gaps and available scopes in this area to utilize the battery system to work in co-ordination with the cathodic protection system for reinforced concrete. In this review paper, in addition to the details and results of the researches related to the cement-based batteries, the parameters for performance assessment of the cementbased battery systems had been discussed with a brief description for better understanding of the outputs reported by various authors who have worked in the area.

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Authors' contributions

The first draft of the manuscript was written by AS and the same was reviewed and changes were informed by PT. Both authors have made a substantial contribution to the manuscript. The authors had read and approved the final manuscript.

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Availability of data and materials

Not applicable.

Declarations

Competing interests

The authors declare that they have no competing interests.

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