Novel enhancement of thin-form-factor galvanic cells: Probing halogenated organic oxidizers and metal anodes

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ABSTRACT

The work reported herein demonstrates a novel method to improve the overall performance of thin-form-factor galvanic cells, fabricated via micro-electromechanical systems (MEMS) processes. Use of solid, low cost, cyclic-halogenated, organic catholyte materials permits water activation of cells consisting of metal anode and catalytic platinum positive electrodes. Similar cells, employing aluminum and zinc anodes, have been activated using sodium hypochlorite (NaClO) solutions, i.e. bleach, in the past. The oxidizers chosen for this study (bromo-, chloro- and iodo-succinimides, and sodium dichloroisocyanuric acid) supply the cathode's oxy-halogenated ions when in contact with water. Zinc, magnesium and aluminum anodes are utilized to fabricate galvanic cells. A comparison between these anodes, coupled with various oxidizers, is included herein. Results using aluminum anode cells show that, even though the utilization efficiency of the catholyte reagents is low (faradic efficiencies between 16 and 19%), the performance of the new water-activated cells ($6\,\text{cm} \times 6\,\text{cm} \times 0.25\,\text{cm}$) is superior when compared to those activated with bleach. For instance, operational lives of 6 h (activation with 10% NaClO solution) increase to more than 30 h using the new approach, with a 100-ohm-load. It is also shown that specific energies of 90–110 Wh kg^{-1} (calculated to include both reagent and packaging mass) could be obtained using the described approach with current draws between 10 and 20 mA. The specific energies obtained suggest that novel MEMS-type cells could have much broader application than low-current, bleach-activated cells.

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1. Introduction

Although cost-effective examples of commercially successful primary (single-time use) and secondary (rechargeable) batteries exist, research and development efforts in electrochemical power sources are still intense [1–6]. A major thrust is the development of power sources for portable and easily deployable instrumentation [4–10]. Galvanic cells of the reserve type (i.e. activated "on demand") offer several advantages for field use that include minimization of self-discharge and potential elimination of heavy pressure housings when used as water-activated batteries in underwater systems [7–9].

Metals with high energy content such as lithium, magnesium, and aluminum, are considered cutting-edge anode materials in the battery industry. Even though lithium has, theoretically, the highest energy density (energy per unit weight), it is not straightforwardly suited for use with aqueous electrolytes. Magnesium is the electron-donor material most traditionally used for water-activated batteries [7–9]. Aluminum, the metal with the highest

specific energy (energy per unit volume), continues to be investigated as a battery anode, including reserve-type applications [10,12–21]. Zinc, a cost-effective anode material widely used in the fabrication of commercial batteries, is typically paired with cathodes such as ammonium chloride, manganese dioxide in alkaline media and, more recently, silver oxide [2,22–24]. Zinc has also been used to fabricate reserve cells with some of the cathodes examined in this study [25–27].

Many oxidants have been coupled with the metal anodes mentioned above; however, the issue of optimizing control of secondary reactions that compete with energy production remains challenging. Various approaches have been devised to address inefficiency issues that prove detrimental to the overall cells' energy content. One approach entails controlled dosage of electrolyte [11,23,24]. Oxidizers such as oxygen, chlorine, and alkaline hydrogen peroxide solutions, in combination with aluminum anodes, continue to appear in fuel-cell-like (or forced-flow type) galvanic systems [11,25,28,29]. In 1994, hypochlorite solution was postulated as a cathode material in magnesium and aluminum cells [30]. In subsequent work, Medeiros et al. sought to develop an underwater powering system using cells that utilized continuously pumped liquid hypochlorite electrolyte [31]. The results indicated that impressive current loads were possible for hypochlorite cell systems.

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Aluminum anode cells, with electrode interspacing on the order of microns, have been recently fabricated and studied [19–21,32–34]. Bleach solutions coupled with Al and Zn in thin-form-factor, MEMS-fabricated cells provided sufficient specific energy and energy densities to power MEMS and/or other low-power-requirement devices [35]. Faradic efficiencies were between 40 and 60% and the energy content attendant to the active cell materials was found to be of the same order of magnitude as those of commercially available batteries (40–120 Wh kg^{-1}) at low current densities (1.4×10^{-2} to 4.9×10^{-2} mA cm^{-2}). However, at larger current densities, the cells' Faradic efficiency and specific energy dropped to 9.5% and 20 Wh kg^{-1}, respectively, for cells with inter-electrode separation in the sub-millimeter range [35]. This manuscript describes (1) the performance of cells containing aluminum and a series of halogenated organic oxidizers, and (2) the performance of cells that contained the best organic oxidizer from the aluminum experiment and a series of metal anodes in thin-form-factor cells [36,37]. The results are compared with those from recently presented hypochlorite-activated cells. It should be noted that in the past, magnesium has been tested with mixtures of carbon powder and several of the solid organic oxidizers [38,39]. This work differs from others in that only relatively pure forms of the oxidizing compounds were used between the electrodes, since it was expected that the sub-millimeter separation of the MEMS-fabricated current collector and the metal anode would provide adequate power outputs without compromising the amount of available oxidizer.

2. Chemistry considerations

The overall chemical reaction between metal anode, M, and hypochlorite-ions is reported to be

$$M_{(s)} + NaClO_{(l)} + H_2O_{(l)} \rightarrow NaCl_{(aq)} + M(OH)_{m(s)} \quad (1)$$
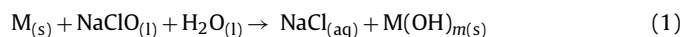
where m represents the oxidation-state change that the metal undergoes [27,30,34]. The reaction implies decomposition of hypochlorite into chloride and hydroxide ions during the cathode half-reaction

$$ClO^-_{(aq)} + H_2O_{(l)} + 2e^- \rightarrow Cl^-_{(aq)} + 2OH^-_{(aq)} \quad (2)$$
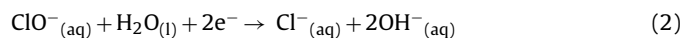
and oxidation of M, releasing m electron-moles per mole of M, in the anode half-reaction [22–37]

$$M_{(s)} \rightarrow M^{m+}_{(aq)} + m\,e^- \quad (3)$$

Solid chlorinated oxidizers have been utilized for organic synthesis and disinfection purposes for almost 40 years [40–42]. One of the most widely accepted mechanisms of disinfection is the formation of oxidizing hypohalogenous acids upon water contact. Studies on the equilibrium constants of both chlorosuccinimide and dichloroisocyanurates have appeared in literature [41,42]. The weak acid dissociation of both the organic oxidizer and the hypohalogeneous acid depends on the pH of the solution as well as temperature, and the combination of these processes results in a chemically complex mixture. Quantification of species in these mixtures may be possible, but certainly not in an expeditious manner, given the dynamic conditions expected within the galvanic cells. Rather than attempting studies to formulate/corroborate the mechanistic steps or kinetics of the cells' chemical reactions, a set of experiments was conducted using the materials in the fabricated cells. A summary of cathode half-reactions for all the organic compounds tested, similar to Eq. (2), can be written as follows.
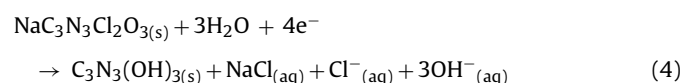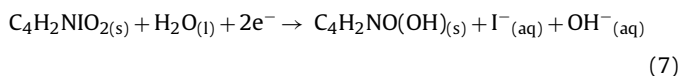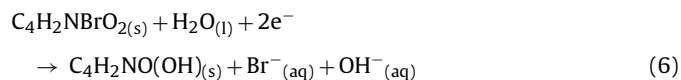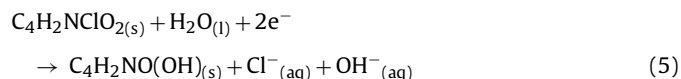
$$NaC_3N_3Cl_2O_{3(s)} + 3H_2O + 4e^-$$
$$\rightarrow C_3N_3(OH)_{3(s)} + NaCl_{(aq)} + Cl^-_{(aq)} + 3OH^-_{(aq)} \quad (4)$$

Table 1
Physicochemical characteristics of solid organic oxidizers and theoretical electrochemical equivalents of galvanic pairs between the oxidizers and three metal anodes

Novel characteristics of the heterocyclic halogenated organic oxidants		Electrochemical equivalents and energetic content[a]			Galvanic cells[b]			
Compound formula/molecular weight (g mol^{-1})	E° (V valence change^{-1})	Charge (Ah g^{-1})	Energy (Wh g^{-1})	Energy (Wh cc^{-1}) (density, g cc^{-1})	Metal anode	E° (V)	Current (Ah g^{-1})	Energy (Wh g^{-1})[1]
Chlorosuccinimide C$_4$H$_4$ClNO$_2$/133.5	0.89/2	0.40	0.36	0.59 (1.65)	Mg / Al / Zn	3.2 / 2.6 / 1.7	0.34 / 0.35 / 0.27	1.09 / 0.92 / 0.46
Bromosuccinimide C$_4$H$_4$BrNO$_2$/178.0	0.76/2	0.30	0.23	0.48 (2.10)	Mg / Al / Zn	3.1 / 2.4 / 1.5	0.26 / 0.28 / 0.22	0.82 / 0.66 / 0.33
Iodosuccinimide C$_4$H$_4$INO$_2$/225.0	0.99/2	0.24	0.24	0.24 (1.0)	Mg / Al / Zn	3.2 / 2.6 / 1.7	0.22 / 0.22 / 0.18	0.69 / 0.57 / 0.31
Sodium-dichloro-s-triazinetrione[c] NaC$_3$N$_3$Cl$_2$O$_3$/219.9	0.89/4	0.49	0.43	0.88 (2.03)	Mg / Al / Zn	3.2 / 2.6 / 1.7	0.40 / 0.42 / 0.31	1.28 / 1.09 / 0.52

[a] Calculated using the shown E° that corresponds to the standard potential value of the reduction of hypohalogenated acid.
[b] Calculated using standard oxidation potentials.
[c] Also known as sodium dichloro-isocyanuric acid.

$$C_4H_2NClO_{2(s)} + H_2O_{(l)} + 2e^-$$
$$\rightarrow C_4H_2NO(OH)_{(s)} + Cl^-{}_{(aq)} + OH^-{}_{(aq)} \qquad (5)$$

$$C_4H_2NBrO_{2(s)} + H_2O_{(l)} + 2e^-$$
$$\rightarrow C_4H_2NO(OH)_{(s)} + Br^-{}_{(aq)} + OH^-{}_{(aq)} \qquad (6)$$

$$C_4H_2NIO_{2(s)} + H_2O_{(l)} + 2e^- \rightarrow C_4H_2NO(OH)_{(s)} + I^-{}_{(aq)} + OH^-{}_{(aq)}$$
$$(7)$$

The chemical Eqs. (4)–(7) indicate that cells can be activated simply by water addition, turning the cell design into a reserve water-activated battery, WAB. Theoretical energetic and current contents of the cells tested are shown in Table 1. It is assumed that chemical reactions of the materials proceed stoichiometrically according to Eqs. (4)–(7) and Eq. (1). However, the presence of a solid metal hydroxide in Eq. (1) depends on the pH of the solution. In the cases of aluminum and zinc, desirable soluble products can be formed within certain ranges of high and low pHs, while magnesium may require an acidic environment [27].

3. Experimental

3.1. Materials, cell fabrication, and protocol

Fig. 1A shows an isometric view (not to scale) of cell components. For the sake of completeness, Fig. 1B shows a process-flow for the fabrication of these cells. Details concerning the microfabrication process can be found elsewhere [33,34]. The resulting thickness of the cells was 0.25 cm and a footprint of 6 cm × 6 cm. The active electrode area was 30 cm². A total of four oxidizer-releasers (heterogeneous halogenated cyclic compounds) were tested with three different metals: magnesium, zinc, and aluminum. The oxidizer-releasers utilized, bromo-, chloro- and iodosuccinimide

(as examples of mono-halogenated compounds), were acquired from Alfa Aesar. Commercially available sodium dichloroisocyanuric acid (also known as sodium dichloro-s-triazinetrione or NadiCl-s-triazinetrione), a common disinfectant in pools [41], was also used as a hypochlorite ion-releaser. The main advantage in the use of these compounds is the extremely low cost when compared to other oxidizers. Relatively inexpensive metal anodes (99.98% purity) were purchased from Alfa Aesar. Rather than fabricating a series of twelve cell-types, coupling each of the four oxidant releasers with each of the three anodes, we followed the ensuing logic to perform a smaller set of experiments. Aluminum was used as the baseline anode to be paired with the three different halogenated compounds. Using the compound that provided the longest operational time with aluminum, other cells were then fabricated with zinc and magnesium anodes. Besides their low cost, these solid oxidizer-releaser materials provide a relatively large amount of oxidizing material (Table 1). The calculated price per available charge ranges from 4 to 40 Ah U.S.$^{-1}$ and the specific capacity varies between 0.40 and 0.49 Ah g^{-1} for the chlorinated compounds. As a comparison, silver chloride, a well established oxidizer used for WABS, contains 0.19 Ah g^{-1} with a price of 0.17 Ah U.S.$^{-1}$ at the time this manuscript was prepared. A Fluke 189 Multimeter was used to record electric potential as a function of time immediately after the cells were filled with either the 10% NaClO solution or tap water.

4. Results and discussion

Figs. 2 and 3 show results obtained with an aluminum anode and three different halogenated oxidizers. Fig. 2 shows polarographic-type curves for each of these cases. It is clear that the cells able to provide the largest potential, current, and power capacity were those fabricated with compounds containing halogens of lighter atomic masses (bromine and chlorine). The brominated compound was able to provide higher electric potentials than those obtained with the chlorinated succinimide for small current draws
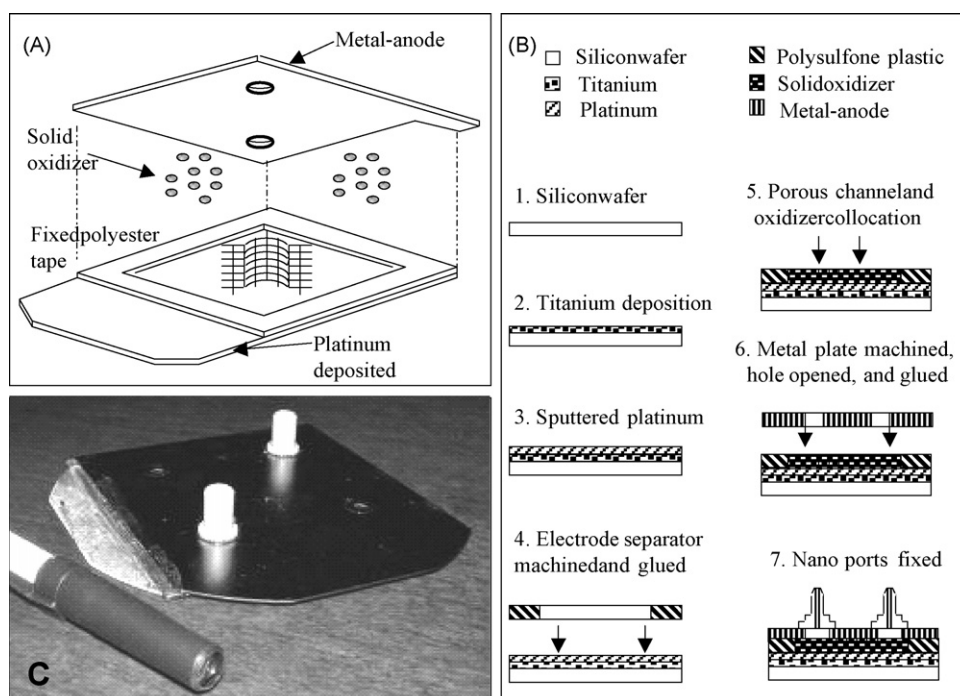

Fig. 1. Assembly of thin-form-factor cells. (A) Isometric view of the cells' structure. (B) Schematic showing the fabrication of the platinum-sputtered current-collector and cell assembly. (C) Insert that shows a picture of one of the fabricated cells with 5.5 cm × 5.5 cm of active electrode areas.
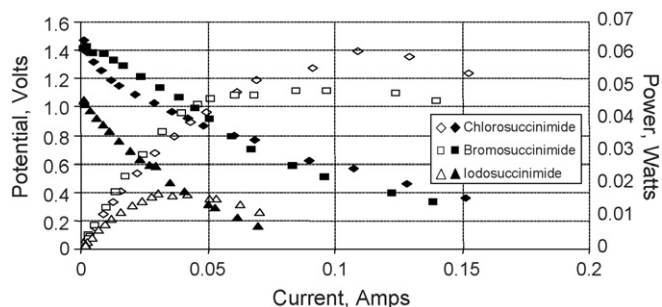
Fig. 2. Performance of aluminum anode cells and halogenated solid oxidizer compounds. Cell potential (filled markers) and power (open markers) delivered vs. current.

Fig. 4. Cell potential (filled markers) and power (open markers) delivered vs. current drawn for aluminum anode cells. The cells were activated with a 10% stabilized sodium hypochlorite solution, or tap water for cells containing two of the solid chlorinated compounds.

(0 < current capacity < 60 mA). However, at currents higher than 60 mA, the chlorosuccinimide compound provided higher potentials and power capacities than the brominated version. The iodated compound clearly exhibited the poorest performance with respect to sustained voltage when compared to the other two halogenated compounds.

Another important dimension is the "operational time" of the cells, that is, the interval during which the cells were able to sustain a constant potential while providing current. The results shown in Fig. 3, obtained with a constant load of 27 ohms, provide insight into this parameter. Even though bromosuccinimide provided large current capacities, its duration was limited to a relatively short time when compared to either one of the two other halogenated compounds. In contrast, while the potential sustained by the chlorosuccinimide was lower than that of bromo-, the overall charge and energy delivered by cells fabricated with the chlorinated oxidizer was considerably higher. A summary of the cell characteristics obtained with tap water activation is shown in Table 2. Interestingly, because of the longer cell-life observed from the cell fabricated with the iodated compound relative to the brominated version, the charge released at the tested resistive load was also slightly higher. The comparison of delivered work, however, revealed that the brominated version provided a larger energetic content. The reason for the superior performance of cells with the chlorinated oxidizer (Table 2) is hypothesized to be due to the solubility of the compound such that it permits rapid establishment of equilibrium between the organic weak acid and the water, as described in Section 2 of this manuscript. The time that is required for establishment of the aforementioned equilibrium, together with diffusion-transfer limitations, common in battery where a moist solid oxidiz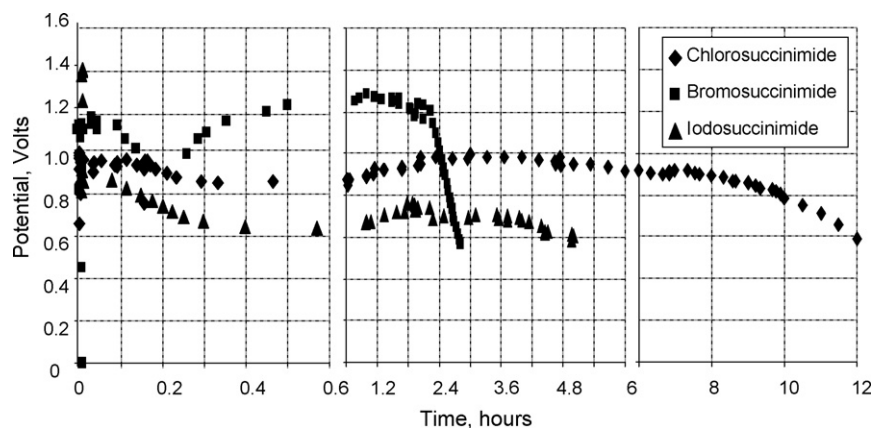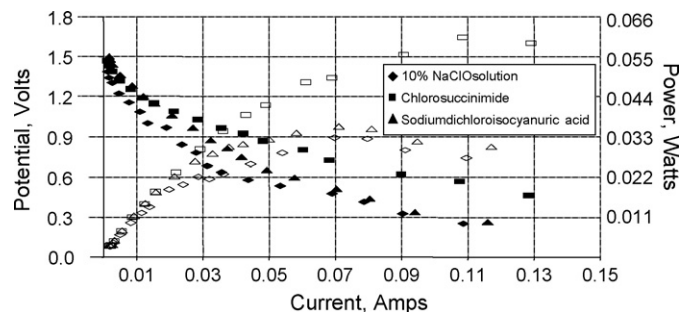er is present, provide a possible explanation for the decrease and subsequent recovery of the potential as a function of time in the early stages of discharge.

A comparison between a monosubstituted oxy-halogenated compound (chlorosuccinimide) and that of a di-halogenated organic acid is presented in Fig. 4. Of the three different oxidants employed, the behaviors of the 10% sodium hypochlorite solution and sodium dichloroisocyanurate were found to be very similar throughout the range of resistors tested. This suggests that the hypochlorous acid (pK_a = 7.46) formed by dissociation of sodium dichloroisocyanurate displays similar oxidizing capacity to that of dissolved hypochlorite ions present in the NaClO-solution. For the case of cells prepared using chlorosuccinimide as the oxidizer, it was found that the maximum power delivered was considerably higher than that obtained with the other two oxidizers. It is important to note, however, that such electrical power was obtained while drawing relatively large current. In fact, power outputs greater than 40 milliwatts were obtained only while the cell was able to sustain voltages lower than 0.8. The fact that chlorosuccinimide provides considerably greater current and power outputs than sodium dichloroisocyanurate throughout the studied range of currents is probably due to the documented capacity of chlorosuccinimide to very quickly transfer chloride ions directly into the oxygen–nitrogen bond of succinimide [41]. In fact, it has been corroborated that the dynamic equilibrium between the succinimide molecules and the chlorinated compound is established faster than that thought to be formed between the chlorosuccinimide and water [42].

Figs. 5 and 6 show typical cell potential outputs as a function of time for tap water (1 mL) activated cells containing 4 g of chlorinated oxidizer-releasers at various resistive loads. As discussed

Fig. 3. Performance of aluminum anode cells and halogenated solid oxidizer compounds. Cell potential vs. time for cells under a 27 ohm-resistive load.

Table 2
Performance of aluminum anode and halogenated succinimide cells activated with water

Halogen	Open voltage (V)	Average potential (V)	Operational time (h)	Total output delivered from cells with an active electrode area of 5.5 cm × 5.5 cm and containing 4 g of organic oxidizer	
				Charge (Ah)	Energy (W h)
Cl	1.60	0.89	12	0.39	0.35
Br	1.49	1.14	2.8	0.12	0.14
I	1.20	0.69	5.0	0.13	0.09

A 27 ohm-load closed the circuit, the cut-off voltage (end of the run) occurs when potential is lower than 0.6 V.
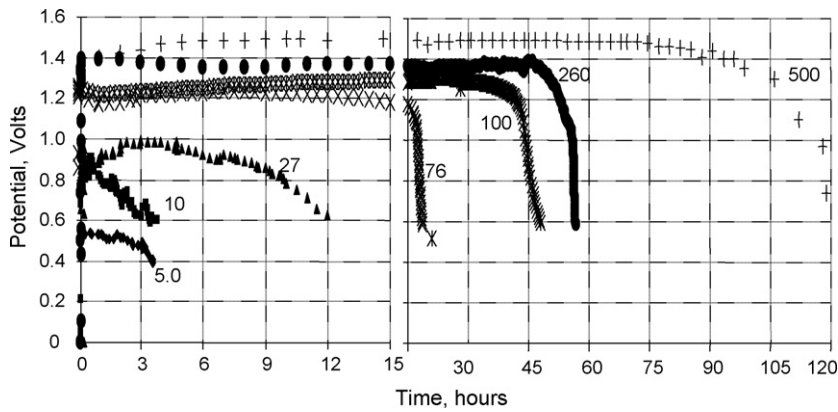
Fig. 5. Comparison of cell potential vs. time at various resistive loads for cells fabricated with an aluminum anode and chlorosuccinimide as the solid organic oxidizer.
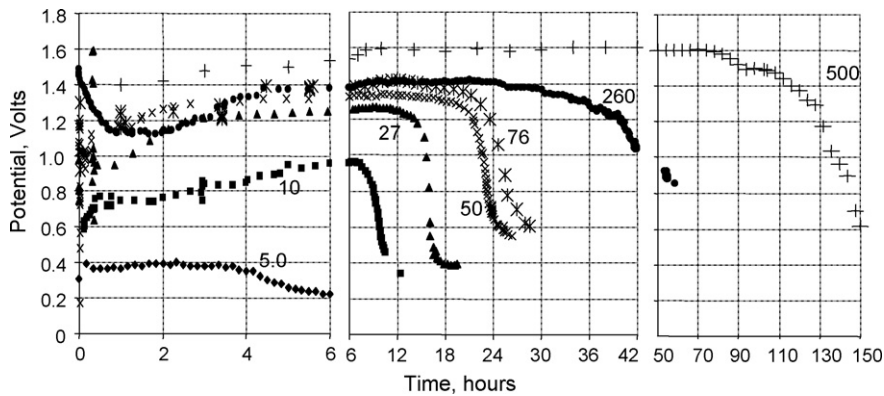
Fig. 6. Comparison of cell potential vs. time at various resistive loads for cells fabricated with an aluminum anode and solid oxidizers. Results from cells where sodium dichloroisocyanuric acid oxidant is used.
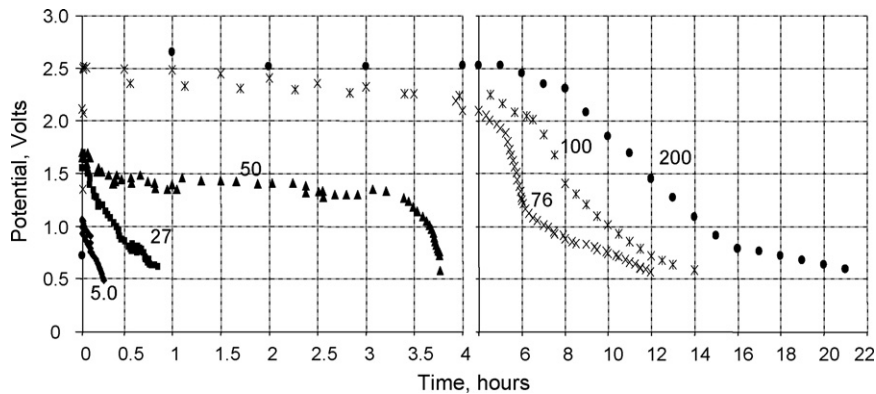
Fig. 7. Cell potential as a function of time for cells assembled with sodium dichloroisocyanuric acid and that use magnesium anodes.
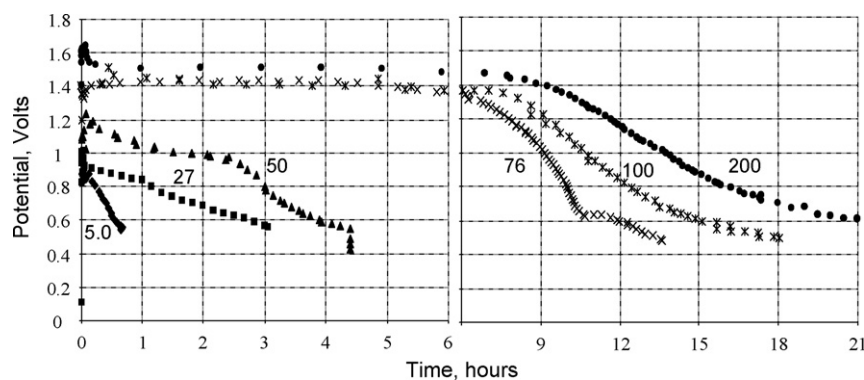
Fig. 8. Cell potential as a function of time for cells assembled with sodium dichloroisocyanuric acid. Zinc metal is utilized as an anode.

above, the figure reveals that at a small load (5 ohms), the potential sustained with the monochlorinated compound is higher than that obtained with the sodium-dichloro compound.

When the cells are subjected to other resistors ($10\,ohms \leq$ resistive loads $\leq 500\,ohms$), the potentials delivered are very similar. Regardless of the measured cell potential, the operational time during which the potential is sustained differs substantially depending on the utilized oxidizer.

In general, it appears that the chlorine content of the oxidizer (oxidizing specie) has an impact on the overall charge transfer and operational time of the cell.

The last set of experiments performed used cells constructed with metal anodes other than aluminum. Figs. 7 and 8 present cell potential curves, as a function of time and with variable loads, obtained from magnesium- and zinc-anode cells, respectively. As expected, given the oxidation potential of magnesium, cells with this anode metal provided higher voltages than those constructed with zinc. It is important to note that, in general, the sustained operational times of cells assembled with zinc anodes are slightly longer than those that used magnesium. If Figs. 6–8 are compared, it is evident that the operational times using aluminum anodes are considerably greater than those obtained with the other two metals. Table 3 shows a comparison between calculated performance-estimators (charge and work delivered, average potential, etc.) from experimental runs similar to the ones presented in Figs.6–8Figs.

6 through 8. The table shows that aluminum reacts with the chlorinated oxidizer for a longer period of time than does either magnesium or zinc. One likely reason, besides intrinsic differences in diffusion rates of reaction products for the three metals, is that aluminum chloride (one of the reactants that can be formed according to the availability of chlorine ions, as indicated by Eqs. (4) and (5)) is known to hydrolyze, forming hydroxy-aluminated complexes. These chemical complexes are soluble when the pH of the solution is slightly acidic. The presence of hypochlorous acid likely maintains a reduced pH, at least during the first stages of the reactions. When zinc and magnesium anodes are utilized, however, a precipitate forms on the surface of the anode. The scales are thought to be magnesium and zinc hydroxides. When the metal anodes are dipped into acidic solutions, the scales dissolve and the metal is then available for use in assembly of other cells.

Table 3 also shows that the lifespan of sustained power outputs at usable sustained voltages is greatly enhanced when using the solid oxidizers as compared to the hypochlorite solutions. In addition, even though the columbic (about 50% for the oxidizers) and the overall Faradic efficiencies (16% with the sodium dichloroisocyanurate and 20% with the chlorosuccinimide) of the galvanic cells are relatively low, the overall specific energy is very attractive ($90–110\,Wh\,kg^{-1}$), since it is of similar magnitude to commercial systems currently used to power deployable instrumentation, including marine and oceanographic equipment [43,44]. In the

Table 3
Summary of cells' performance at selected loads

Cells–galvanic pair (observed open voltage (V))	Average potential (volts (load ohms)$^{-1}$)	Operational time (h)	Actual electrochemical equivalents & energetic content with respect to the active materials only (gravimetric efficiency (%))		Actual electrochemical equivalents & energetic content estimated including the actual cells' body, packaging and dimensions		
			Charge (Ah kg^{-1})	Energy (Wh kg^{-1})	Charge (Ah kg^{-1})	Energy (Wh kg^{-1})	Energy (Wh L^{-1})
Al–NaOCl[a]	0.97/100	5.8	43.8 (62)	42.5 (23.1)	11.7	11.4	15.2
	1.42/5k	155	19.2 (48.5)	48.7 (26.5)	9.2	13.0	18.4
Al–C$_4$H$_4$ClNO$_2$	0.74/10	3.8	65 (19.0)	48.6 (5.2)	35.9	26.8	59.8
	0.88/27	12	91.2 (26.1)	81.4 (8.8)	50.3	44.9	100
	1.23/100	48	136.0 (38.9)	169.1 (18.4)	75.0	93.2	208
Al–C$_4$H$_4$BrNO$_2$	1.14/27	2.8	27.6 (9.9)	32.2 (5.6)	15.2	17.7	39.5
Al–C$_4$H$_4$INO$_2$	0.69/27	5	29.7 (13.5)	20.6 (3.1)	16.4	11.4	25.3
Al–NaC$_3$N$_3$ Cl$_2$O$_3$	0.75/10	12.4	216 (51)	174 (16.0)	119.2	95.9	214
	1.06/27	19.5	177 (42)	203 (18.6)	97.6	111.5	249
	1.23/50	25.9	148 (35)	184 (16.8)	81.3	101.2	225
Mg–NaC$_3$N$_3$ Cl$_2$O$_3$	1.03/27	0.85	7.45 (7.45)	8.3 (0.65)	6.6	4.6	10.2
	1.61/100	14	51.0 (12.7)	97.33 (7.6)	28.1	53.7	119.6
Zn–NaC$_3$N$_3$ Cl$_2$O$_3$	0.75/27	3.06	19.7 (6.33)	14.9 (2.9)	10.8	8.3	18.4
	1.15/100	18.1	100.2 (32.3)	86.9 (16.7)	55.2	47.9	106.8

Four grams of solid organic oxidizer was encased within the cells, cell's active electrode area is $30\,cm^2$.

[a] 10% stabilized solution. The values from these rows were taken from Ref. [35].

past, specific energies between 40 and 120 Wh kg^{-1} were found for cells activated with hypochlorite ions [34]. In the present work, if only the materials involved in the reactions are considered, values between 170–200 Wh kg^{-1} are obtained. If one uses carbon foil rather than silicon wafer, the approximate weight of cell packaging is 3.5 g, for a total weight cell of about 8–9 g. This value was used when calculating the specific energies that included cell packaging shown in Table 3. In order to compare with small commercial water-activated batteries, the reader is reminded that batteries comprised of two or more (11–16) cells are the most common commercially available designs. If one considers individual magnesium–silver chloride cells on a commercial battery, the estimated weight per cell is 22 g, and its dimensions are 7.5 cm × 5.5 cm × 0.39 cm. The specific energy and energy density of these magnesium–silver chloride, water-activated cells are reported to be 130 Wh kg^{-1} and 204 Wh L^{-1}, respectively [2].

The values of both specific energy and energy density of the aluminum anode reported cells is two orders of magnitude higher when the cells are compared to those activated with sodium hypochlorite solutions, if the calculation is confined to the constitutive basic materials. These results are of the same order of magnitude as those of commercial cells that are currently used in deployments of scientific instrumentation in marine sciences.

5. Conclusions and final considerations

A new approach for enhancing power output and energy content of thin-form-factor, MEMS fabricated reserve batteries is described herein. The advantages of utilizing a solid catholyte releaser are manifold. Firstly, the specific energy was increased substantially when compared to cells activated with bleach solution. Also, when comparing the operational lives of the cells subjected to similar loads, the performance of the described novel approach is largely superior to that of cells activated with 10% sodium hypochlorite solutions. Additionally, the solid material should be easier to package than a gaseous cathode releaser [28,29]. This, together with the fact that they are water-activated, makes the cells attractive for marine applications. The results show that by using different oxidizers, a relatively wide range of potential and current draws are possible, making the cells versatile for a variety of powering applications and a wider set of applications (those that do not necessarily require relatively small current draws) than the MEMS aluminum cells reported so far [34].

Current and future work includes evaluation of additional inexpensive, water-activated cathode materials as well as probing alternative means for increasing their efficiency. Also, mechanical micro valves and vents are currently being developed for the development of automated batteries [45,46].

References

[1] R.J. Broad, Interface 8 (1999) 20–23.
[2] D. Linden, T.B. Reddy, Handbook of Batteries, third ed., McGraw-Hill Handbooks, New York and other Cities, 2002, pp. xix-xx and 1.11-24.23.
[3] W.A. van Schalkwijk, B. Scrosati (Eds.), Advances in Lithium-ion Batteries, Kluwer Academic/Plenum Publishers, New York and other Cities, 2002.
[4] S. Wasmus, A. Küver, J. Electroanal. Chem. 461 (1999) 14–31.
[5] C.K. Dyer, J. Power Sources 106 (2002) 31–34.
[6] N.S. Sisworahardjo, M.S. Alam, G. Aydinli, J. Power Sources 177 (2008) 412–418.
[7] A.G. Ritchie, N.E. Bagshaw, Phil. Transact.: Mathem., Phys. Eng. Sci. 354 (1996) 1643–1652.
[8] B.N. Adams "Batteries" U.S. Patent 2,322,210 (1943).
[9] H.N. Honer, F.P. Malaspina, W. J.Marini, "Lead chloride Electrode for Seawater Batteries" U.S. Patent 3,943,004 (1976).
[10] M.G. Medeiros, C.G. Zoski, J. Phys. Chem. B. 102 (1998) 9908–9914.
[11] M.G. Medeiros, E.G. Dow, J. Power Sources 80 (1999) 78–82.
[12] S. Zaromb, J. Electrochem. Soc. 109 (1962) 1125–1130.
[13] S. Licht, C. Marsh, J. Electrochem. Soc. 139 (1992) L109–L111.
[14] D. Peramunage, S. Licht, Science 261 (1993) 1029–1032.
[15] S. Licht, D. Peramunage, J. Electrochem. Soc. 140 (1993) L4–L6.
[16] D. Peramunage, R. Dillon, S. Licht, J. Power Sources 45 (1993) 311–323.
[17] S. Licht, N. Myung, J. Electrochem. Soc. 142 (1995) L179–L182.
[18] Q. Li, N.J. Bjerrum, J. Power Sources 110 (2002) 1–10.
[19] V.R. Challa, A.M. Cardenas-Valencia, R.F. Benson, L. Langebrake, S. Bhansali, Eurosensors 2002, Prague, Czech Republic, September 15–18 2002.
[20] A.M. Cardenas-Valencia, D. Fries, H. Broadbent, L. Langebrake, R.F. Benson, Proc. Volume, µTAS 2003, The 7th International Conference on Miniaturized Chemical and BioChemical Analysis Systems, 1, 2003, pp. 311–314.
[21] A.M. Cardenas-Valencia, D.P. Fries, G. Steimle, H. Broadbent, L.C. Langebrake, R.F. Benson, First International Conference on Fuel Cell Science, Engineering and Technology, NY, USA, 2003, pp. 279–286.
[22] K.W. Whiten, K.D. Gailey, R.E. Davis, General Chemistry with Qualitative Analysis, third ed., Saunders college publishing, 1988, pp. 631–632.
[23] A.P. Karpinski, S.J. Russell, J.R. Serenyi, J.P. Murphy, J. Power Sources 91 (2000) 77–82.
[24] E.J. Settembre (Army electronics Command, Fort Monmouth N J), High Energy, Long-life, Zinc-Silver oxide secondary battery, Research and development technical report, June 1970.
[25] C. Marsh, S. Licht, J. Electrochem. Soc. 141 (1994) L61–L63.
[26] E.G. Dow, R.R. Bessette, G.L. Seeback, C. Marsh-Orndorff, H. Meunier, J. VanZee, M.G. Medeiros, J. Power Sources 65 (1997) 207–212.
[27] M.G. Medeiros, R.R. Bessette, C.M. Deschenes, C.J. Patrissi, L.G. Carreiro, S.P. Tucker, D.W. Atwater, J. Power Sources 136 (2004) 226–231.
[28] S. Yang, H. Knickle, J. Power Sources 112 (2002) 162–173.
[29] J.-F. Equey, S. Müller, A. Tsukada, O. Haas, J. Appl. Electrochem. 19 (1989) 65–68.
[30] A. Brenner, J. Electrochem. Soc. 143 (1996) 3133–3138.
[31] M.G. Medeiros, R.R. Bessette, C.M. Deschenes, D.W. Atwater, J. Power Sources 96 (2001) 236–239.
[32] A.M. Cardenas-Valencia, V.R. Challa, D. Fries, L. Langebrake, R.F. Benson, S. Bhansali, Sens. Actuat. B: Chem. 95 (2003) 406–413.
[33] A.M. Cardenas-Valencia, J. Dlutowski, J. Bumgarner, L. Langebrake, W. Moreno, J. Micromech. Microeng. 16 (2006) 1511–1518.
[34] A.M. Cardenas-Valencia, J. Dlutowski, J. Bumgarner, S. Knighton, C. Biver, L. Langebrake, Sens. Actuat. B: Chem. 122 (2007) 328–336.
[35] A.M. Cardenas-Valencia, C.J. Biver, L. Langebrake, J. Power Sources 166 (2007) 273–283.
[36] A.M. Cardenas-Valencia, L. Langebrake, J. Dlutowski, M. Calves, J. Bumgarner, Micro-Aluminum Galvanic Cells and Method for Constructing the Same, Invention disclosure submitted to Division of Patents and Licensing USF, Serial No. 60/596,071, May 2005.
[37] A.M. Cardenas-Valencia, C.J. Biver, L. Langebrake, J. Bumgarner, Novel Materials to Supply Oxy-halogenated Ion to be used as part of enhanced power Sources, Invention disclosure submitted to USF, Reference Number 06A047PR, April 2006.
[38] M.J. Pollack, Corporate author: Honeywell Inc. Horsham PA, Power Sources Center, Low Cost Water Activated Reserve Battery, ADA008053, DTIC, February 1974.
[39] D.P. Bhatt, S. Karthikeyan, R. Udhayan, J. Electrochem. Soc. 139 (1992) 3019–3024.
[40] S.D. Worley, W.B. Wheatley, H.H. Kohl, H.D. Burkett, J.A. Van Hoose, Ind. Eng. Chem. Prod. Res. Dev. 22 (1983) 716–718.
[41] A. Hussain, T. Higuchi, A. Hurwitz, I.H. Pitman, J. Pharmac. Sci. 61 (1972) 371–374.
[42] M.L. Pinsky, H.-C. Hu, Environ. Sci. Technol. 15 (1981) 423–430.
[43] G.P.G. Kibelka, R.T. Short, S.K. Toler, J.E. Edkins, R.H. Byrne, Talanta 64 (2004) 961–969.
[44] L.R. Adornato, E.A. Kaltenbacher, D.R. Greenhow, R.H. Byrne, Environ. Sci. Technol. 41 (2007) 4045–4052.
[45] A.M. Cardenas-Valencia, J. Dlutowski, J. Bumgarner, W. Wang, R. Popuri, L. Langebrake, Sens. Actuat.: A. Phys., 136 (1) 374–384.
[46] M.L. Cardenas, A.M. Cardenas-Valencia, J. Bumgarner, L. Langebrake, J. Micromech. Microeng. 17 (2007) 1671–1679.