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High capacity aqueous periodate batteries featuring a nine-electron transfer process

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Abstract

We present sodium manganese periodate (NaMnIO_6) as a novel cathode material, which exhibited a nine-electron discharge process, for the development of high-performance aqueous battery systems. Purified carbon nanotubes (CNTs) were selected as conductive cathode additive. Along with an anion exchange membrane, acid-salt water dual electrolytes were used to reduce anode corrosion. NaMnIO_6 showed a specific capacity as high as 750 mAh g^{-1} in prototype batteries, which was nearly 94% of the theoretical capacity. Different anode metals were studied and the Mg system showed the highest specific energy of 746 Wh kg^{-1} . Furthermore, these batteries fabricated using 3D-printed casings also feature replaceable electrodes once they are consumed.

Keywords

Periodate; Aqueous battery; 3D-printing; Anion exchange membrane; Carbon nanotubes

1. Introduction

High energy density, specific capacity, safety, low toxicity and costs are important considerations in electrochemical energy storage [1]. Many conventional batteries such as zinc-based ones are based on single-electron cathode processes [1]; cathode materials with high valence can achieve multi-electron processes thus increasing specific capacity. Periodates offer such possibility of multi-electron discharge processes. Insoluble manganese-based salts and metal oxides have been widely used as electrode materials: LiMn_2O_4 is a common cathode for lithiumion batteries [2–4] and supercapacitors [5,6]; MnO_2 serves as electrodes in zinc-carbon [7], alkaline batteries [8–11], and super-capacitors [12–14]. Periodates with discharge from IO_4^- to IO_3^- [15,16] in alkaline electrolytes, and IO_3^- based electrodes [17,18] with the final reduction to I_2 in acidic electrolytes, were reported.

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Author contributions

Z. Wang made the batteries and studied their properties. Z. Wang, K. Chen and X. Meng performed material preparation and characterization. Z. Wang and S. Mitra developed the concepts and prepared the manuscript.

Declarations of interest

None.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ensm.2019.02.021>.

In general, both Mn(IV) and I(VII) are oxidizing, making their complex a potential material for the multi-electron process in electrodes. Compounds such as NaMnIO₆ and KMnIO₆ are microcrystalline solids, insoluble in water, stable under normal conditions [19], which may hold promise as electrochemical materials.

As seen in Fig. 1a, materials with higher specific capacities are for lithium battery systems, which use organic electrolytes. O₂ and S are promising electrodes for aqueous systems, yet the former is unsuitable for high power output due to the low concentration of O₂ in the air; S based aqueous systems showed low output voltage and hence specific energy [20]. Solid cathodes with high specific capacity for aqueous systems are yet to be developed. In Mn-containing periodates, specifically NaMnIO₆, Mn(IV) can be reduced to Mn²⁺ [21] while I(VII) can be reduced to I₂ through a 9-electron process, giving a theoretical specific capacity of 802 mAh g⁻¹, higher than most of the metal salts and oxides. This would lead to the development of high capacity aqueous battery systems.

The objective of this paper is to develop electrochemical systems based on NaMnIO₆ that are optimized for premium performance. Another objective is to further explore the synthesis conditions and properties of NaMnIO₆.

2. Materials and methods

2.1. Materials synthesis and treatment

Standard NaMnIO₆ for battery cathodes was prepared via reaction between MnSO₄ (monohydrate, Sigma Aldrich, 99%) and NaIO₄ (Honeywell, meta, 99%) solutions. 100 mL 0.1 M MnSO₄ was added into 400 mL 0.05 M NaIO₄ at the rate of 1 mL min⁻¹. The solution was stirred during the process and stirring was continued for another 30 min. The precipitate was filtered, washed using Milli-Q water, and then dried under vacuum. The purification of carbon nanotubes (CNTs, multiwalled, purity 95%, Cheap Tubes Inc. Brattleboro, VT, USA) was performed in a Microwave Accelerated Reaction System (Mode: CEM Mars) using 1 M HNO₃ as previously reported [6].

2.2. Batteries in 3D-printed casings

The optimized cathode contained 19.86% purified CNTs, 6% polyvinylpyrrolidone (PVP, Sigma Aldrich, average mol wt. 10000), and 74.14% NaMnIO₆. Cathodes were controlled at 0.016 g with an area of 2.4 cm × 1.4 cm. Zinc foils (3 cm × 2 cm, 0.57 g, in excess, Metalnastri, Italy) served as anodes unless otherwise mentioned.

Carbon cloth was used as cathode current collectors. Current collector was stuck onto the adhesive side of ethylene vinyl acetate (EVA) resin coated polyethylene terephthalate (PET) before cathode slurry was pasted and dried under vacuum. Then a hydrophilic polytetrafluoro-ethylene (PTFE, 5.0 μm, ANOW) film was placed on cathode and laminated to form the cathode assembly.

Single electrolyte systems contained 15 mL 6 M HAc electrolyte (Fig. 2a&b), while dual-electrolyte batteries contained 4.5 mL 1 M HCl and 8.5 mL 1 M NaCl (Fig. 2c), separated by FuMA-Tech Fumasep FAB-PK-130 anion exchange membranes. 3D-printed battery

casings were fabricated using polylactic acid (PLA) plastic in a Flashforge Creator Pro 3D Printer. The anion exchange membrane was then inserted, followed by electrodes, before electrolytes were injected (Fig. 3a).

2.3. Stoichiometrically optimized cells

In order to improve the specific energy of cells, mass of electrodes was optimized according to the stoichiometry of the redox reactions. Besides Zn, Al (TWP inc., 120 Mesh Aluminum 5056, 0.004" Wire Dia) and Mg (Wrinkly, 99.95%, Ribbon) were used as anodes (0.066 g Zn, Fig. 3c; 0.02 g Al, Fig. 3d; 0.0325 g Mg, Fig. 3e). The cathodes weighed 0.04 g, containing 19.86% purified CNT, 6% PVP and 74.14% NaMnIO₆, with an area of 2.4 cm × 1.4 cm. 8.5 mL 1 M HCl and 4.5 mL 1 M NaCl was used as cathode and anode electrolytes, respectively. Fabrication methods were the same as previously mentioned batteries in 3D-printed casings.

2.4. Testing and characterization

The electrochemical performance of the cells was measured using 8-channel MTI Battery Analyzers. The assembled cells were discharged using constant current methods. Scanning electron microscopy (SEM) with Energy-dispersive X-ray spectroscopy (EDX) were collected on an LEO 1530 VP Scanning Electron Microscope. Thermogravimetric analysis (TGA) was done on a PerkinElmer Pyris 1. Cyclic voltammetry (CV) was carried out on a Homiangz 320C electrochemical analyzer versus a standard Ag-AgCl electrode in 1 M HCl electrolyte. During the cyclic voltammetry (CV) analysis, the working electrodes had a similar composition to the regular battery electrode, except that PVP was replaced by PTFE (Sigma Aldrich, preparation, 60wt% dispersion in water).

3. Results and discussion

3.1. Material characterization and cathode development

The sodium manganese periodates were prepared by titration of MnSO₄ into NaIO₄ solution, which not only provided IO₄⁻ anions but also served as an oxidizing agent.

Synthesized periodate complex was dark red in color (Fig. 1), in line with what had been reported before [19]. According to scanning electron microscopy (SEM) images, the sample comprised of sub-micron spherical crystals. Energy-dispersive X-ray spectroscopy (EDX) showed the presence of Na, I, Mn, and O. Thermogravimetric analysis (TGA) showed that the compound was relatively stable below 250 °C. The minor gradual drop was attributed to the removal of residue and crystallization water. More details can be found in Ref. [22]. Several synthetic processes were tested (See Table 1 in Ref. [22]). Direct addition of MnSO₄ into NaIO₄ was the best approach and showed the most desired Na:Mn:I atomic ratio of 1:1:1. NaMnIO₆ also showed larger capacity than compounds with other formulas (See Fig. 2 in Ref. [22]). The cathode formula was optimized regarding carbon conductive additives. An optimum formulation containing 19.86% purified CNTs, 6% polyvinylpyrrolidone (PVP) and 74.14% NaMnIO₆ was used in the following studies (Fig. 3 in Ref. [22]). There has been a trend to make metal oxide/salt-carbon composite for electrode applications [23–

25]. Yet it was found that in presence of carbon, larger particles with undesired Na:Mn:I atomic ratio was obtained (Figure 4 and Table 2 in Ref. [22]).

3.2. Batteries fabricated with 3D-printing

3.2.1. Cells using HAc electrolyte—Space was limited in Swagelok-type cells while zinc was corroded in acid, generating H_2 and consuming electrolyte. To add sufficient electrolyte (Fig. 2a), we fabricated cells in 3D-printed battery casings [26]. The dark red $NaMnIO_6$ disappeared during the discharge process. Starch test showed that I_2 was produced from I(VII) reduction, which was in line with a previous report [26]. During the discharge, Zn atoms were oxidized to Zn^{2+} , which dissolved in the electrolyte (Fig. 2b). A discharge plateau was observed around 1.3 V with the following proposed reaction: neutrality when anode Zn is converted to Zn^{2+} .

The HAc electrolyte led to anode corrosion, which significantly limited the performance under low discharge rates. We developed a dual-electrolyte system composed of an acidic electrolyte (HCl) at cathode and a neutral electrolyte (NaCl) at anode. The resulted batteries showed much higher discharge plateau compared to HAc, providing higher output power (Fig. 2c). This was also in line with our previous report where higher H^+ concentration led to higher working voltage in periodate electrodes [26]. Furthermore, even for low-rate discharge, the batteries avoided failing due to zinc depletion. The batteries showed capacities at around 9 mAh (equivalent to $750 \text{ mAh g}^{-1} NaMnIO_6$),

When discharged at 0.3 mA, the battery showed a capacity of 7.24 mAh ($608.2 \text{ mAh g}^{-1} NaMnIO_6$). However at 0.2 mA, discharge voltage dropped fast after 22 h and finally failed when zinc anode was exhausted. The capacity of HAc cells was dependent on discharge rates: faster discharge delivered larger capacity before electrolyte and anode were consumed by side reactions.

3.2.2. Acid-salt dual-electrolyte batteries—Dual-electrolyte/dual-ion designs offer several advantages. In some systems, both anions and cations are involved in electrochemical processes [27–30], which improves working voltage and cell performance. Alternatively, in a single electrochemical cell where one electrode requires specific ions that should be prevented from reaching the other electrode, dual-electrolyte designs block the undesired ions. In our study, H^+ cations would benefit cathode process but should be avoided at the anode; while anions such as Cl^- are required to maintain electrical nearly 94% of the theoretical capacity. We observed that faster discharges delivered more capacity. Since acid and anode were not limiting reagents, a possible explanation was a slow redox reaction between I(VII) and Cl^- . Different polymers were tested as additives in the cathode, and PVP was found to be a better choice compared with others (Fig. S1a).

Cyclic voltammetry is presented in Fig. 2d&e. During the scan from 1.6 V to 0 V, cathode peaks were observed at around 1.05 V, 0.7 V and 0.3 V, which were attributed to the reduction of I(VII), Mn(IV) and I(V), respectively [21,31]. Two anode peaks much smaller than the corresponding cathode peaks were also observed. As cycling continued, the oxidation peaks decreased or even disappeared (Fig. 2e), indicating reactions with poor reversibility. However, the reduction peak of Mn(IV) decreased first and then increased and moved towards lower potential. It was inferred that the increase was due to the regeneration of Mn(IV) in the form of MnO₂ [21]. The asymmetric shapes of the cyclic voltammograms indicated that NaMnIO₆ was more suitable for primary batteries in acidic electrolytes. Cyclic voltammetry was also used to test HAc electrolyte; however since HAc was a very weak electrolyte, no peak could be observed.

The fabrication process of such dual-electrolyte batteries is exhibited in Fig. 3a. The structural components were 3D-printed before the anion exchange membrane, electrodes were inserted and electrolytes were added. Fig. 3b shows the mechanism. The anion exchange membrane blocked the migration of H⁺ inhibiting reaction between zinc and the acid. Anions can move freely, completing the circuit. The chemical reaction is as below:

The NaMnIO₆ particles disappeared during the discharge process and yellowish brown color formation was observed on the cathode side, which was attributed to the generation of I₂. This was confirmed using a starch indicator which formed dark blue color upon adding into the electrolyte. Quantitative analysis of I₂ in the spent electrolyte was carried out using UV-vis spectroscopy (Supplementary Text and Fig. S2). 78% of the iodine present in the original electrode was recovered as I₂, demonstrating that I₂ was a major product of the discharge reaction. It has been reported that in addition to the electrodes, the ions can also be supplied by the electrolyte [28]; consequently, the concentrations of the electrolytes could be critical factors. Different concentrations of HCl were tested (Fig. S1b). A higher acid concentration led to a higher output voltage but lowered the capacity due to side reactions.

3.3. Anodes and battery rate performance

Cells containing stoichiometric quantities of anode metals namely Zn, Al, Mg were fabricated. NaMnIO₆ showed the highest specific capacity of around 750 mAh g⁻¹. The discharge voltage dropped when the anode was no longer in significant excess (Figs. 2c and 3c); specific capacity also dropped under high discharge rates, which was attributed to the limited anode surface area. The passivation layer on Al surface was hard to dissolve in neutral electrolyte, which significantly dropped the output potential below 1.1 V under higher discharge rates (Fig. 3d). However, due to the higher specific capacity and low density, Al cells showed higher specific energy. Mg brought the highest output voltage and hence specific energy (746 Wh kg⁻¹, calculated based on active materials in both electrodes, Fig. 3e). However, the self-corrosion was significantly enhanced when discharged, especially under high rates. In corrosive NaCl solution, all the above metals were subject to

corrosion, generating hydrogen and OH^- . Yet this was more critical in Mg cells, for bubbles were generated during discharge; higher anode current enhanced corrosion [32]. Low concentrations of NaCl were tested as electrolytes for Mg cells but showed no further improvement. We believe that corrosion inhibitors and Mg alloys could potentially address this issue. Table 1 shows the rate performance of all the above-mentioned cells.

4. Conclusions

High capacity aqueous batteries have been developed. The cathode material, NaMnIO_6 was prepared by precipitation reaction of MnSO_4 and NaIO_4 , and was then used for the first time in battery applications. A 3D-printed reserve battery design comprising of acid-salt dual electrolyte system was also developed. NaMnIO_6 showed a high specific capacity of 750 mAh g^{-1} which was 94% of its theoretical capacity. Together with Mg anode, the highest specific energy reached was 746 Wh kg^{-1} . In our opinion, higher performance can be achieved with further optimization of electrolyte, anode and anion exchange membrane with higher proton blocking. It is conceivable that other types of electrochemical cells can be also developed based on periodate chemistry presented here.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. NaMnIO₆ nanoparticle characterization: (a) Theoretical specific capacity; (b) & (c) SEM images; (d) TGA; (e) EDX and photograph.

Fig. 2. NaMnIO₆ batteries in 3D-printed casings: (a)&(b) HAc electrolyte; (c) HCl-NaCl dual-electrolyte; cyclic voltammetry in 1M HCl vs Ag-AgCl electrode: (d) different scan rates; (e) cycling properties at 50 mV s⁻¹.

Fig. 3. Battery design and fabrication: (a) Fabrication of a 3D-printed dual-electrolyte battery; (b) schematic diagram of dual-electrolyte design; stoichiometrically optimized battery rate performance: (c) Zn cells; (d) Al cells; (e) Mg cells.

Table 1

Rate properties of NaMnIO₆ batteries using various metal anodes.

Rate		1 C	0.4 C	0.2 C	0.1 C	0.05 C
Zn Cells	Specific Capacity (based on NaMnIO ₆ , mAh g ⁻¹)	664	758	755	748	733
	Specific Energy (based on electrode active materials, Wh kg ⁻¹)	205	302	316	343	337
Al Cells	Specific Capacity (based on NaMnIO ₆ , mAh g ⁻¹)	–	629	697	692	706
	Specific Energy (based on electrode active materials, Wh kg ⁻¹)	–	397	461	505	558
Mg Cells	Specific Capacity (based on NaMnIO ₆ , mAh g ⁻¹)	491	736	738	756	734
	Specific Energy (based on electrode active materials, Wh kg ⁻¹)	343	667	708	746	734