Data Article

Data related to the synthesis, characterization and electrochemical performance of high capacity sodium manganese periodate electrodes

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ABSTRACT

Sodium manganese periodate compounds were synthesized to serve as high capacity cathodes. The composition and morphology of resulting products were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray Diffraction (XRD) and thermogravimetric analysis (TGA). Composite cathodes made from the synthesized periodates were used to fabricate batteries with zinc anode and acetic acid electrolyte. Electrode formulations were optimized using nanocarbon conductive additives. For the full design and mechanism related to the sodium manganese periodate electrode with specific capacity as high as 750 mAh g⁻¹, please refer to our research article “High Capacity Aqueous Periodate Batteries Featuring a Nine-Electron Transfer Process” [1].

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1. Data

1.1. The synthesis of different periodates

The analysis of differently synthesized periodates is presented in Table 1. Periodate-carbon nanotube as well periodate-graphene oxide-carbon nanotube composites were also synthesized. Byproducts could also be produced during the NaMnIO6 synthesis process. Introducing other oxidizing reagent or even carbon materials appeared to enhance these reactions. Na2S2O8 was tried as a co-oxidizing reagent and it was found that MnO2 was produced as an undesired byproduct. The atomic (molar) ratios of Na:Mn:I were determined using energy-dispersive X-ray spectroscopy (EDX), and the formula was developed from these results. Table 1 presents the formula of different products synthesized in our study and the corresponding synthesis methods, where A and B are the starting materials. Carbon nanotubes (CNTs) and graphene oxide (GO) was also used to prepare periodate-nanocarbon composites.

1.2. Characterization of the synthesized periodates

Both Na0.1Mn2.4O6.1O5.2 and Na2Mn2.4IO9.3 had sub-micron sizes according to the scanning electron microscopy (SEM) images (Fig. 1a&b), similar to NaMnIO6 (see Fig. 1b&c in Ref. [1]). With very small amount of Na and I, Na0.1Mn2.4O6.1O5.2 was similar to MnO2 and less dependent on H+ during discharge. A favorable synthesis method for NaMnIO6 was the direct addition of MnSO4 into NaIO4. Resulted products were purified, characterized and made into battery cathodes. The batteries were discharged and the datasets of discharge properties were collected.

Fig. 1c shows the X-ray Diffraction (XRD) pattern for NaMnIO6. The sample showed hexagonal crystalline structures with space group P312 (ICDD 00-023-0685). Major peaks at 17.21°, 20.52°, 26.92°, 35.88°, 40.08°, 45.40°, 50.96°, 59.14°, 64.45°, 67.24° were assigned to (001), (100), (101), (110), (111).
### Table 1
The synthesized products, starting materials and synthesis methods.

| Sample             | A                                      | B                                      | method                                      |
|--------------------|-----------------------------------------|-----------------------------------------|---------------------------------------------|
| \( \text{Na}_0 \text{Mn}_2 \cdot \text{IO}_3 \cdot \text{O}_{5.2} \) | 400 mL water                           | 3.422 g NaIO₄ in 100 mL water            | Add B into A at 1 mL min⁻¹, 80 °C            |
|                    | 1.812 g MnSO₄                           | 8 g Na₂S₂O₈                             |                                             |
|                    | 1 mL 1 M H₂SO₄                          | 1.69 g MnSO₄ in 100 mL water            |                                             |
| \( \text{Na}_2 \text{Mn}_2 \cdot \text{IO}_{9.3} \) | 400 mL water                           | 1.812 g MnSO₄ in 100 mL water            | Add B into A at 1 mL min⁻¹, 80 °C            |
|                    | 3.422 g NaIO₄                           | 8 g Na₂S₂O₈                             |                                             |
|                    | 1 mL 1 M H₂SO₄                          | 1.69 g MnSO₄ in 100 mL water            |                                             |
| \( \text{NaMnIO}_6 \)   | 400 mL water                           | 4.278 g NaIO₄ (0.05 M)                 | Add B into A at 1 mL min⁻¹, Room temperature |
| periodate-CNT       | 400 mL water                           | 50 mL 0.1 M MnSO₄                       | Sonicate A for 60 min, Add B into A at 1 mL min⁻¹, Room temperature |
|                    | 2.139 g NaIO₄                           |                                         |                                             |
|                    | 0.4 g CNT                               |                                         |                                             |
| periodate-CNT-GO    | 400 mL water                           | 50 mL 0.1 M MnSO₄                       | Sonicate A for 60 min, Add B into A at 1 mL min⁻¹, Room temperature |
|                    | 2.139 g NaIO₄                           |                                         |                                             |
|                    | 0.4 g CNT                               |                                         |                                             |
|                    | 10 mL GO                                |                                         |                                             |

**Fig. 1.** SEM images of (a) \( \text{Na}_0 \text{Mn}_2 \cdot \text{IO}_3 \cdot \text{O}_{5.2} \) and (b) \( \text{Na}_2 \text{Mn}_2 \cdot \text{IO}_{9.3} \); (c) XRD Pattern of NaMnIO₆.
Thermogravimetric analysis (TGA) showed that NaMnIO₆ remained stable below 250 °C (Fig. 1d in Ref. [1]).

1.3. Discharge performances for different cells using periodate cathodes

Discharge curves (Fig. 2) plotted from datasets showed the discharge properties of Swagelok-type cells fabricated using different periodate cathodes, zinc foil anodes, 6 M HAc electrolyte, PTFE and glass fiber separator. The composition of periodate had an impact on battery performance. Although the initial discharge potential increased with higher MnO₂ amount, the total capacity dropped. The NaMnIO₆ cell lasted around 13 hr (3.909 mAh capacity, 305 mAh g⁻¹), showing better capacity; however, these were far from the theoretical values. This was attributed to the limited space in Swagelok cells and direct reaction between zinc and acid.

1.4. Cathode formulation optimization using nanocarbons

Nanocarbons are conductive, physically and chemically stable, and have high surface areas along with improved dispersibility. These features make them suitable conductive additives [2,3]. Cathode formulation was optimized with HAc electrolyte and zinc anode to determine the type and amount of the conductive additives. Purified CNTs were found to be the best option (Fig. 3a) and the quantity was optimized (Fig. 3b). It was found that the presence of impurities such as metal oxides enhanced side reactions [4]. Discharge curves from datasets showed that a larger amount of carbon additives enhanced electrode conductivity but took up valuable space in electrodes; 19.86% of purified CNTs was found to be the optimum amount (Fig. 3b).

1.5. Synthesis of sodium manganese periodate-nanocarbon composites via in situ precipitation

During in situ precipitation, the conductive carbon served as the scaffolds on which the insoluble periodates were loaded via redox-precipitative reaction. The expected advantage of this approach was that there would be good contact between the conductive additive and reactive reagent, facilitating electron migration and transfer. In addition, the high surface area of nanocarbons would be well utilized. Here, periodate-CNT and periodate-CNT-GO composites were prepared. However, the performance was lower compared to the simple mixing of periodate with the

![Graph showing discharge curves for different cells using periodate cathodes](image-url)

**Fig. 2.** Swagelok cells using sodium manganese periodate compound cathodes, zinc anode and 6 M HAc electrolyte.
nanocarbons. SEM images (Fig. 4b-e) showed that in presence of carbon materials, sodium manganese periodate aggregated significantly and formed larger particles. Furthermore, EDX dataset (Table 2) showed the atomic ratios of Na:Mn:I in these composites were different from the ideal 1:1:1 ratio, which was attributed to side reactions between NaIO₄ and the impurities and functional groups on carbons.

1.6. Functional 3D-printed batteries made using periodate electrodes

3D-printed reserve batteries with NaMnIO₆ electrodes are shown in Fig. 5. The specific capacity reached as high as 750 mAh g⁻¹, which was one of the highest ever reported for a primary battery [1].

2. Experimental design, materials and methods

2.1. Material synthesis and treatment

Different synthesis methods for sodium manganese periodate was tried and are listed in Table 1, where A and B were the starting reactants. Besides NaIO₄ (Honeywell, meta, ≥ 99%), Na₂S₂O₈ (LOUDWOLF Industry & Scientific, ≥ 98%) was also used as the oxidizer. Resulting solid was filtered, washed with water and dried under vacuum overnight. Periodate-carbon composites were prepared by similar methods with carbon nanotubes (CNTs, multiwalled, purity 95%, Cheap Tubes Inc. Brattleboro, VT, USA) and/or graphene oxide (GO, Graphenea, 0.4 wt%) pre-added into A. Some CNTs were treated in a Microwave Accelerated Reaction System (Mode: CEM Mars) using 1 M HNO₃ to remove amorphous carbons and metal oxide residues [5]. The resulted samples were referred to as purified CNTs.

2.2. Swagelok-type electrochemical cell fabrication

Batteries were fabricated in Swagelok-type cells using stainless steel current collectors (MTI, Richmond, CA) and assembly was made with a PTFE film (5.0 μm, ANOW) and a glass fiber separator (Grade GF/A: 1.6 μm, Whatman) sandwiched between electrodes. Cathodes containing 80% periodate, 14% carbon and 6% polyvinylpyrrolidone (PVP, Sigma Aldrich, average mol wt. 10000) were used to evaluate the performance of different sodium manganese periodates. For the composites containing nanocarbons, electrode contained 6% PVP, with the rest periodate-carbon composites. Cells were fabricated using 0.48 g zinc foil anode (Metalnastri, Italy) and 6 M HAc electrolyte, with dry cathode of 0.016 g, which was the limiting reagent.
2.3. Cathode formulation optimization

Optimization was carried out in Swagelok-type cells. Cathode formulation of 80% periodate, 14% carbon and 6% PVP was used to select the proper nanocarbon additive: raw CNTs without treatment, Fig. 4. (a) Cell performance of carbon-periodate complexes; SEM images of (b)&(c) CNT-GO-periodate composite; (d)&(e) CNT-periodate composite.

Table 2
EDX results for periodate-carbon composites.

| Element | CNT-periodate weight % | CNT-periodate atomic ratio | CNT-GO-periodate weight % | CNT-GO-periodate atomic ratio |
|---------|------------------------|----------------------------|---------------------------|-------------------------------|
| Na      | 4.18                   | 0.68                       | 5.08                      | 1.23                          |
| Mn      | 16.42                  | 1.10                       | 10.72                     | 1.07                          |
| I       | 34.02                  | 1                          | 22.74                     | 1                             |

2.3. Cathode formulation optimization

Optimization was carried out in Swagelok-type cells. Cathode formulation of 80% periodate, 14% carbon and 6% PVP was used to select the proper nanocarbon additive: raw CNTs without treatment,
purified CNTs, and graphitized carbon black (Sigma Aldrich, < 500 nm) were tried as the conductive additives. Once the best carbon type was established, the amount of conductive additives were varied by changing the amount of carbon and periodate, with 6% PVP fixed as the binder (Fig. 3). Cells with periodate-carbon composite cathodes were also fabricated in Swagelok Cells, with 6% PVP and the rest periodate-carbon composites. Again, cells were fabricated using 0.48 g zinc anode and 6 M HAc electrolyte, with dry cathode of 0.016 g, which was the limiting reagent.

2.4. Battery testing

All Swagelok cells were discharged on an MTI 8-channel Battery Analyzer at the constant current of 0.3 mA with the cut off voltage of 0.8 V.

Conflict of interest

None.

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