

Nurul Huda Yusoff *,
Nur Izzah Abd Aze,
Nurhafizah Najmi,
and Mohd Ali Sulaiman.

Industrial Centre of Innovation,
Energy Management,
SIRIM Berhad, Lot 34 Jalan Hi-Tech 2/3,
Kulim Hi-Tech Park, 09000 Kulim, Kedah,
Malaysia

*nuruly@sirim.my

STUDY ON LIQUID ELECTROLYTE USING NaClO_4 SALT FOR LOW COST RECHARGEABLE SODIUM-ION BATTERIES

RINGKASAN: Kertas kerja ini menjelaskan penggunaan cecair elektrolit yang mengandungi garam NaClO_4 untuk kegunaan bateri berteknologi natrium ion yang boleh di cas berulang kali pada kos rendah. Natrium elektrolit, NaClO_4 telah disediakan dengan campuran garam NaClO_4 ke dalam pelarut organik pada variasi kepekatan dan campuran pelarut organik. Sampel elektrolit ini diuji menggunakan alat konduksi meter dan voltametri sapuan linear (LSV). Prestasi elektrolit NaClO_4 dalam peranti sel separuh dengan bahan katod telah diuji menggunakan galvanometer di antara 2.5 V dan 4.0 V pada kadar C/10 pada suhu bilik. Elektrolit NaClO_4 menunjukkan kekonduksian terbaik pada 10.71 mS/cm dalam pelarut organik, ethilena karbonat (EC) and dimethyl carbonate (DMC) dengan nisbah 1:1 sebagai campuran terbaik. Bateri berteknologi natrium ion mempunyai kapasiti hampir 100 mAh/g yang berpotensi untuk menggantikan teknologi bateri litium ion (140 mAh/g) pada kos yang jauh lebih murah

Kata kunci: Cecair electrolit, bateri natrium ion, NaClO_4 .

ABSTRACT: This paper explores the possibilities of using liquid electrolyte containing NaClO_4 salt for application of low cost rechargeable sodium-ion batteries. Sodium electrolyte, NaClO_4 was prepared by the addition of NaClO_4 salt into organic solvent at various concentration and mixture of organic solvent. The samples were tested using electrochemical analytical meter and Linear Sweep Voltammetry, LSV. The performance of NaClO_4 electrolyte in half cell configuration with working cathode material were galvanostatically cycled between 2.5 V and 4.0 V at C/10 rate using an automatic galvanostatic charge-discharge unit at room temperature. The NaClO_4 electrolyte showed promising result with conductivity at 10.71 mS/cm in organic solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) with 1:1 ratio as the best mixture. For cell performance, the Na-ion battery can be cycled near to capacity of 100 mAh/g which has potential to replace lithium-ion battery technology (140 mAh/g) with much cheaper cost.

Keywords: Liquid electrolyte, sodium- ion batteries, NaClO_4

INTRODUCTION

Sodium-ion batteries are the new potential alternative to lithium-ion batteries. In order to replace lithium, sodium seems to be the best alternative as the element is almost similar to lithium. This is because they belong together in Group 1 element where they have one electron in the outer shell, thus having similar properties. In addition, the source of sodium is abundant, which effectively will lead to cost reduction of the batteries especially during the large scale production (Kim *et al.*, 2012). However, the battery performance is still not at par with lithium ion batteries. Thus, a lot of research should be done to produce high capacity rechargeable sodium ion battery at lower cost (Ellis *et al.*, 2012, Kruk *et al.*, 2011, Xiohua *et al.*, 2011 and Ding *et al.*, 2011). The cost of lithium-based electrode material is around \$15,000 a ton, while sodium-based electrode material costs only \$150 a ton (<https://news.stanford.edu/2017/10/09/sodium-based-batteries-cost-effective-lithium>).

One of crucial part of sodium-ion batteries research is the development of stable electrolyte. Electrolyte, as an indispensable part of batteries, which offers ion conduction and transport media between the cathode and anode. The safety issues of batteries also lie on the properties of the electrolyte. Optimizing the electrolyte is important for the actual application of sodium-ion batteries (Bhide *et al.*, 2014). Electrolytes can be grouped into four categories: organic electrolytes, ionic liquid, aqueous electrolytes, and solid or polymer-based electrolytes. However, common carbonate based electrolytic solutions are the most widely investigated. Generally, the salts employed in sodium-ion battery have the same anions used in the field of Lithium ion batteries technology (LIBs), including (ClO₄⁻), (PF₆⁻), (BF₄⁻), (CF₃SO₃⁻) and ([N(CF₃SO₂)₂]) such as NaPF₆ (Bhide *et al.*, 2014), NaClO₄ (Ponrouch *et al.*, 2013), NaTFSI (Monti *et al.*, 2014), NaBF₄ (Bordet *et al.*, 2015).

This report explored the possibility on using NaClO₄ salt in liquid electrolytes for low cost sodium-ion batteries application. The report will focus on the conductivity and electrochemical stability of NaClO₄ salt in the organic solvent at different concentration and mixture variation of the organic solvents. The compatibility performance with working cathode material of sodium vanadium phosphate, Na₃V₂PO₄ was studied in half-cell configuration.

MATERIALS AND METHOD

Electrolyte preparation

NaClO₄ base liquid electrolyte was prepared by mixing sodium perchlorate, NaClO₄ (Aldrich, 98%) at concentration ranging from 0.8 M, 1.0 M and 1.2 M in the selected organic solvent of ethylene carbonate, EC (Aldrich, 99%, anhydrous), diethyl carbonate, DEC (Aldrich, 99%), dimethylene carbonate, DMC (Aldrich, 99%, anhydrous) and propylene carbonate, PC (Aldrich, 99.5%). The electrolytes were mixed into binary and ternary system. All solvents were used as received. All the solutions electrolytes were prepared in a glove box and tested for conductivity using electrochemical analytical meter using Mettler Toledo S70 Advanced Conductivity Meter.

The electrochemical window stability of the electrolytes was studied by Linear Sweep Voltammetry (LSV) via CH Instrument Electrochemical Analyzer. The LSV was performed in a glass bottle using flooded technique where two stainless steel rods as an electrode for anode and cathode respectively. The distances between both electrodes were 5 mm. The measurements of the LSV in the range of 0 to 4 V were performed in a glove box in a controlled environment to avoid any contamination. This cell setup was used to simulate the real battery configuration.

For preparation of half-cell configuration batteries, of Na₃V₂PO₄ cathodes material, 1.0 M of NaClO₄ electrolyte and separator was used and then assembled in a coin cell with sodium metal as the anode. Sodium vanadium phosphate, Na₃V₂PO₄ were prepared by sol gel method by mixing of sodium carbonate, Na₂CO₃ (purity 99.8%), vanadium (V) oxide, V₂O₅ (purity 99.0%) and ammonium dihydrogenphosphate, NH₄H₂PO₄ (purity 99.0%) into aqueous citric acid solution (Song *et al.*, 2014). The cells were galvanostatically cycled between 2.5 and 4.0 V at C/10 rate using galvanostatic charge-discharge unit (WBCS3000 battery cycler, WonA Tech. Co.) at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the ionic conductivity result of prepared NaClO₄ based liquid electrolyte in various concentrations and mixture of organic solvents. It was found that, 1.0 M NaClO₄ in 1:1 EC: DMC provide the best conductivity of 10.71 mS/cm. Meanwhile, the lowest conductivity was 7.05 mS/cm from the mixture of 0.8 M NaClO₄ in 1:1:1 EC: DEC: DMC. The optimised conductivity was achieved at 1.0 M of

NaClO_4 in EC: DMC due to sufficient conductive ion in the mixture of EC and DMC at precise viscosities (Ponrouch *et al.*, 2013). However, at increasing concentration at 1.2 M of NaClO_4 the viscosity of the electrolyte also increased. As a result, the ions transfer inside this electrolyte concentration slightly reduced due to inefficient movement of electron. According to the Stokes-Einstein Law for diffusion in solution, the relation between molecular movement and diffusion is inversely proportional to the viscosity of the solution (Miller, 1924). Hence, the electrolyte ionic conductivity (molecular movement) is reliant on the viscosity of the solvent system.

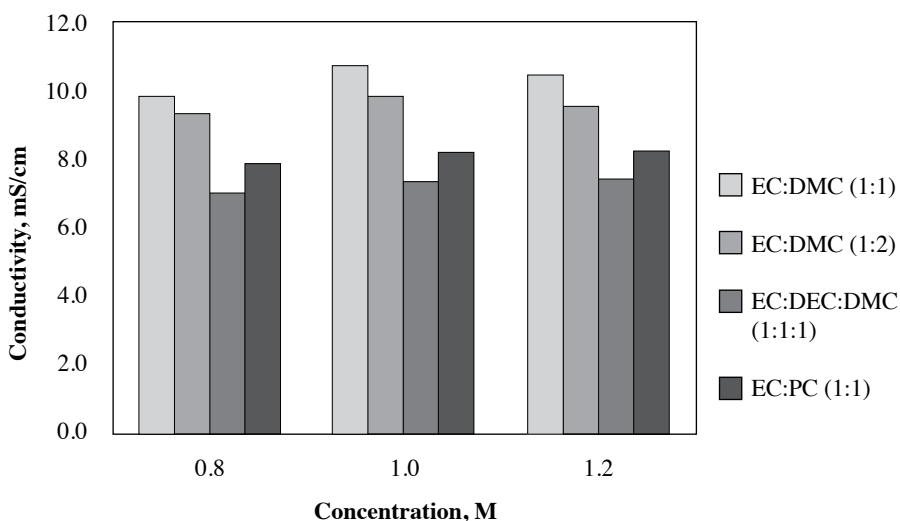


Figure 1. Ionic conductivity of prepared NaClO_4 electrolyte in various concentrations and mixture of organic solvent

Figure 2 shows the window stability of NaClO_4 electrolyte in 1:1 EC: DMC at various concentrations of 0.8 M, 1.0 M and 1.2 M at a scan rate of 0.01V/s. The electrolyte was selected for this experiment due to the best mixture as discussed. The outcome indicates all electrolytes are stable at the operating window of 3.0 V. Upon reaching the 3.0 V, the electrochemical reaction at the the electrode/electrolyte interface was observed. Figure 3 shows the window stability of 1.0 M NaClO_4 in 1:1 EC: DMC in repetitive run until 5th cycle. It was observed that the electrolytes were stable even after a few runs.

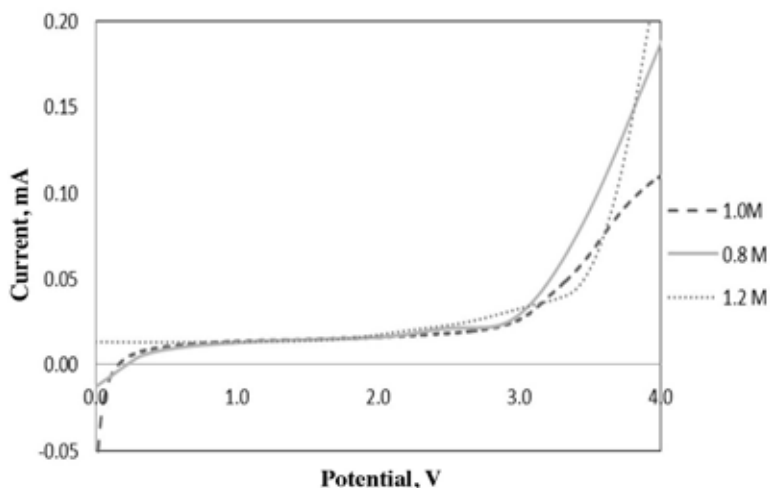


Figure 2. Window stability of NaClO_4 electrolyte in 1:1 EC:DMC at concentration 0.8 M, 1.0 M and 1.2 M

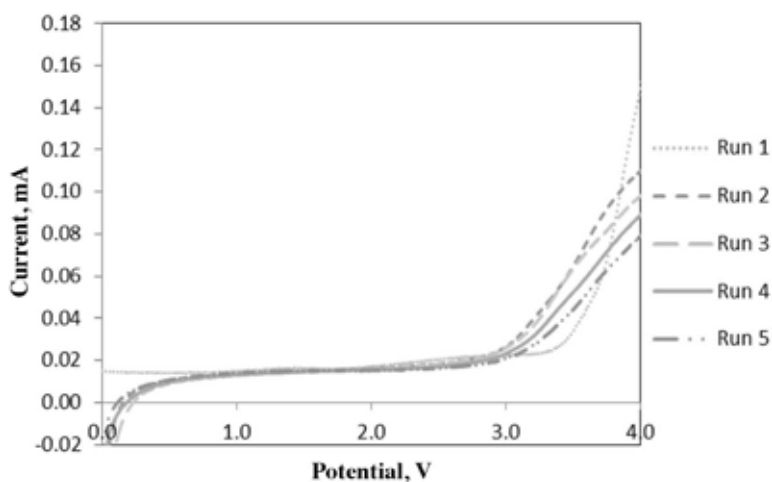


Figure 3. Window stability of 1.0 M NaClO_4 in 1:1 EC:DMC in repetitive run until 5th cycle

Figure 4 shows the discharge curves of 1.0 M NaClO_4 in 1:1 EC: DMC in half cell configuration with working cathode material, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$. The specific capacity recorded for the first cycle at 96.8 mAh/g and the cell demonstrated a stable condition even until 10th cycle with the capacity drop of 6 %.

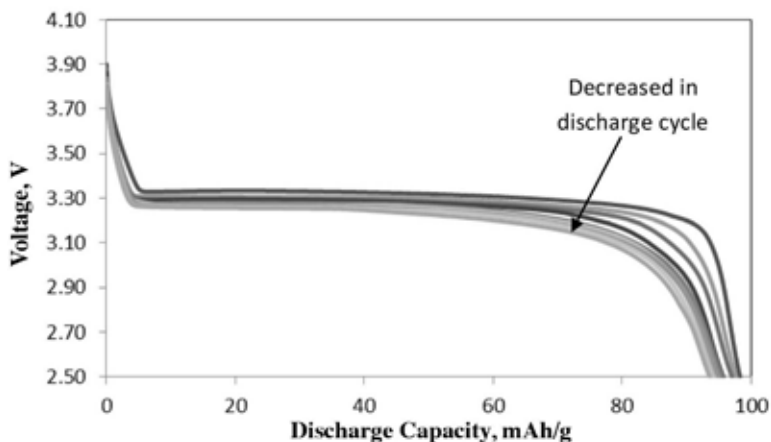


Figure 4. Discharge curve of optimized 1.0 M NaClO₄ in 1:1 EC:DMC in half cell with working cathode material, Na₃V₂(PO₄)₃

CONCLUSION

The NaClO₄ electrolytes were successfully prepared by using NaClO₄ salt at concentrations of 0.8 M, 1.0 M and 1.2 M in the mixture of organic solvent with choices of ethylene carbonate, diethyl carbonate, dimethylene carbonate and propylene carbonate, into binary and ternary systems. It was found that 1.0 M NaClO₄ in 1:1 EC:DMC delivered the optimum conductivity at 10.71 mS/cm. The Na-ion battery can be cycled near to a capacity of 100 mAh/g which is potential alternative to lithium-ion battery technology (140 mAh/g).

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