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CONDUCTIVITY AND ELECTROCHEMICAL STUDY OF NON AQUEOUS NaPF$_6$ ELECTROLYTE IN ORGANIC SOLVENT MIXTURE FOR SODIUM-ION BATTERIES

RINGKASAN: Penyelidikan ini difokuskan kepada kekonduksian dan kajian elektrokimia untuk larutan elektrolit natrium heksafluorofosfat, NaPF$_6$ melalui campuran larutan organik ke dalam sistem sekunder dan tertiar etilena karbonat (EC), dietil karbonat (DEC), dimetilena karbonat (DMC) and propilena karbonat (PC). Kekonduksian ionik dan kestabilan elektrokimia telah dikaji menggunakan meter konduksi termaju dan voltammetri sapuan linear (LSV), masing-masing pada suhu bilik. Pemanasan garam NaPF$_6$ dan pelarut EC dibuat dalam nitrogen atmosfera. Sistem elektrolit NaPF$_6$ dengan EC dan DMC (1:1) telah menghasilkan kekonduksian ionik yang tinggi iaitu 13.14 mS/cm, manakala sistem elektrolit NaPF$_6$ dalam EC dan PC (1:1) telah menghasilkan kekonduksian yang sedikit rendah iaitu 7.72 mS/cm. Voltan sel setengah menggunakan natrium vanadium phosphate, Na$_3$V$_2$PO$_4$ sebagai katod bagi elektrolit optimum telah diuji menggunakan galvanometer pada suhu bilik.

Kata kunci: Electrolit bukan akueus, electrolit bateri natrium ion, NaPF$_6$

ABSTRACT: In this research, we focus on conductivity and electrochemical study of sodium hexafluorophosphate (NaPF$_6$) electrolyte solution prepared with a mixture of various organic solvent consisting of ethylene carbonate (EC), diethyl carbonate (DEC), dimethylene carbonate (DMC) and propylene carbonate (PC) into binary and ternary system. The ionic conductivity and electrochemical window stability were studied using advanced conductivity meter and Linear Sweep Voltammetry (LSV) respectively at room temperature. The binary system of NaPF$_6$ electrolyte with EC and DMC (1:1) had resulted in the highest ionic conductivity at 13.14 mS/cm, while the binary system of NaPF$_6$ electrolyte in EC and PC (1:1) had lowest conductivity at 7.72 mS/cm. The highest capacity of 89.25 mAhg^{-1} was obtained from 1.0 M NaPF$_6$ in of EC and DMC (1:1), while the capacity of 76.07 mAhg^{-1} was obtained using 1.2 M NaPF$_6$ in of EC and DMC (1:1). Half-cell configuration of optimised electrolyte using sodium vanadium phosphate, Na$_3$V$_2$PO$_4$, as working cathode were galvanostatically cycled at room temperature.

Keywords: Non-aqueous electrolyte, sodium-ion battery electrolyte, NaPF$_6$

INTRODUCTION

Lithium-ion battery technology had been successfully exploited for various large-scale energy storage as well as portable electronic devices in these few decades. Nevertheless, the supplies of this material are very limited and inadequate to satisfy the need for various applications. The demand for the material had increased up to more than 12 % a year despite the increasing rates using recycling materials (http://www.thefinancialist.com/spark/the-precious-mobile-metal). Over the years, the price of lithium become expensive. Thus, an alternative to lithium-ion battery system is essential, resulting the utilisation of sodium as a candidate to replace lithium in rechargeable battery technology. Although the performance of the battery system is not comparable to those of lithium ion battery technology, the application had been proven and suitable for large-scale energy storage. Published research reports from various researchers and institutions around the globe have shown that the performance of sodium ion batteries can even surpassed the nickel-metal hydride or lead acids accumulators (Dong *et al.*, 2016). Beside the performance consideration, sodium as a starting material is easily and readily available in abundance as well as much low in cost compared to lithium. 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).

Numerous type of electrolytes had been developed including liquid based (aqueous and non-aqueous), polymer gel and solid electrolytes. However, non-aqueous organic solvent based electrolytes are favourable as they produced high ionic conductivity as well as wide operating voltage window (Vignarooban *et al.*, 2016). The broad usage of organic solvents as an electrolyte in lithium-ion and sodium-ion battery system is due to electrochemical window stability properties. Most of the organic solvents exhibit around 3.5 V of window stability, which can be suitably engineered for application of most electronic devices.

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. Preparation of a binary and ternary solvent system is essential for obtaining an electrolyte with low viscosity, hence improving the ions movement in the electrochemical temperature system. To be useful in the battery application, the electrolytes must provide good ionic conductivity, and must be stable in a wide potential and range (Ponrouch *et al.*,
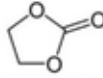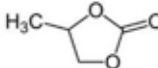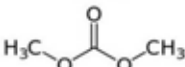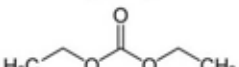
2013). Thus, instead of using a single component solvent, a mixture of carefully matched solvents system is used in practical applications. The rationale behind this mixed solvent formulation is that the diverse and often contradicting requirements of battery applications can hardly be met by any individual compound. In this study, organic carbonates were chosen not only due to their abilities to dissolve sodium salts, but mainly because of their conducting properties for lithium ion batteries.

MATERIALS AND METHOD

Electrolyte preparation

All solvents (≥ 99.0% pure) were obtained from Aldrich and used as received, except for EC, which was heated at 70 °C for 3 hours in nitrogen atmosphere prior being used. Sodium hexafluorophosphate, NaPF$_6$ was obtained from Aldrich (purity 98.0 %) and dried under nitrogen atmosphere at 80 °C prior being used. Electrolyte solutions were prepared using ethylene carbonate (EC), diethyl carbonate (DEC), dimethylene carbonate (DMC) and propylene carbonate (PC). The sample preparations were carried out in a glovebox (<1 ppm H$_2$O) under a nitrogen atmosphere at room temperature in Nalgene bottles for 24 h. Table 1 lists the physicochemical properties of solvents used in this paper (Li *et al.*, 2016).

Table 1. The physicochemical properties of solvents used in preparation of electrolyte

Solvent	Molar Mass, gmol^{-1}	Density, gcm^{-3} (25 °C)	Melting Point, °C	Boiling Point, °C	Flash Point, °C	E_{homo}, eV	E_{lumo}, eV
Ethylene Carbonate (EC)	88	1.32 (40 °C)	36	238	143	−12.86	1.51
Propylene Carbonate (PC)	102	1.2	−49	242	138	−12.72	1.52
Dimethyl Carbonate (DMC)	90	1.06	5	90	17	−12.85	1.88
Diethyl Carbonate (DEC)	118	0.97	−74	127	25	−12.59	1.93

Ionic Conductivity Measurement

Organic solvent of EC, DMC and PC were selected as the solvents mixture for binary solvents system. The ratio of 1:1 volume percentage were selected for EC and DMC as well as EC and PC. On the other hand, the ratio of 1:2 volume percentage were selected for EC and DMC. Organic solvent of EC, DEC and DMC were selected for ternary solvents system with ratio of 1:1:1 volume percentage. NaPF$_6$ was added with solvents mixture at concentration ranging from 0.8 M, 1.0 M and 1.2 M, respectively. The sample measurements were carried out in a glovebox (<1 ppm H$_2$O) under a nitrogen atmosphere at room temperature. The ionic conductivity of the solution was measured with Mettler Toledo S70 Advanced Conductivity Meter.

Electrochemical Window Stability Measurement

Linear Sweep Voltammetry is an important technique for characterisation of electrochemical cell. The technique is performed by sweeping a potential in one linear direction at a predefined voltage ranging from 0 to 0.4 V in two electrodes cell setup at a scan rate of 10 mV/s. This cell setup was used to simulate the real battery configuration. The electrochemical window stability was studied using Linear Sweep Voltammetry (LSV) by CH Instrument Electrochemical Analyzer. The LSV was conducted in a glass bottle using 2 electrodes testing system without reference electrode whereby inert stainless steel was used for both electrodes. The optimised electrolyte was assembled using coin-type half cells method with sodium vanadium phosphate (Na$_3$V$_2$PO$_4$) and sodium metal as cathode and anode, respectively. All the cathode materials obtained from Kanto Chemical were prepared via sol-gel method by sequential addition of stoichiometric ratio of sodium carbonate, Na$_2$CO$_3$ (purity 99.8%), vanadium (V) oxide, V$_2$O$_5$ (purity 99.0%) and ammonium dihydrogenphosphate, NH$_4$H$_2$PO$_4$ (purity 99.0%) into aqueous citric acid solution (Song *et al.*, 2014). The electrochemical performance was studied galvanostatically using WBCS3000 battery cycler at room temperature.

RESULTS AND DISCUSSION

Ionic Conductivity

Figure 1 indicates the ionic conductivity of the prepared non-aqueous electrolytes. The electrolyte consisting of 1.2 M of NaPF$_6$ in EC:DMC showed the highest ionic conductivity at 13.14 mS/cm followed by 1.0 M of NaPF$_6$ in EC:DMC at 12.14 mS/cm, respectively. Meanwhile, the lowest ionic conductivity was obtained by 0.8 M of NaPF$_6$ in EC:PC at 7.72 mS/cm.

Dielectric constant of ionic liquids is influenced by molecular polarization as well as orientation polarisation effected by permanent dipole moments of the ions (Izgorodina *et al.*, 2009). Only molecules with permanent dipole moments are producing orientation polarisation and this is reflected on ionic conductivity. EC is a transparent crystalline solid at room temperature with molecular dipole moment of 4.9 D. High polarity of EC helps forming an efficient solvation shell around sodium ions, thus resulting in highly conductive electrolyte (Aurbach *et al.*, 1999). Since EC is solid at room temperature, EC must be added with linear carbonates or other solvents to yield a liquid electrolyte.

The addition of linear carbonates is essential in producing low viscosity solution. Thus, the addition of a second solvent such as DMC in EC will produce an electrolyte with low viscosity. This is due to the simple linear molecular structure of DMC and its lower density. However, as the ratio of DMC to EC increased by one magnitude, the ionic conductivity of the electrolyte is slightly reduced to 12.00 mS/cm for 1M NaPF$_6$ and 11.75 mS/cm for 1.2M NaPF$_6$. This is due to the decreasing of orientation polarisation effect as DMC consists of small dipole moment, which is at 0.93 D.

The addition of DEC in relation to mixed solvents system of EC and DMC has resulted in decreasing ionic conductivity of 12.30 mS/cm to 9.91 mS/cm for 1M NaPF$_6$. Even though the viscosity of DEC is lower than that of DMC, the molecular formula is bigger with addition of two alkyl group. This reduced the orientation polarisation in the electrolyte, thus reducing the ionic transfer number. Meanwhile, PC is a non-linear carbonate with a molecular dipole moment of 4.9 D, but higher in viscosity compared to DMC. The addition of one methyl group in PC hindered the ionic transfer and reduce the orientation of polarisation of electrolyte. As a result, the ionic conductivity of 1.0 M of NaPF$_6$ in EC:PC electrolyte is lowered due to the increasing ratio of empty space than electric flux to charge. The trend resulted by these electrolytes system is shown in Figure 1.
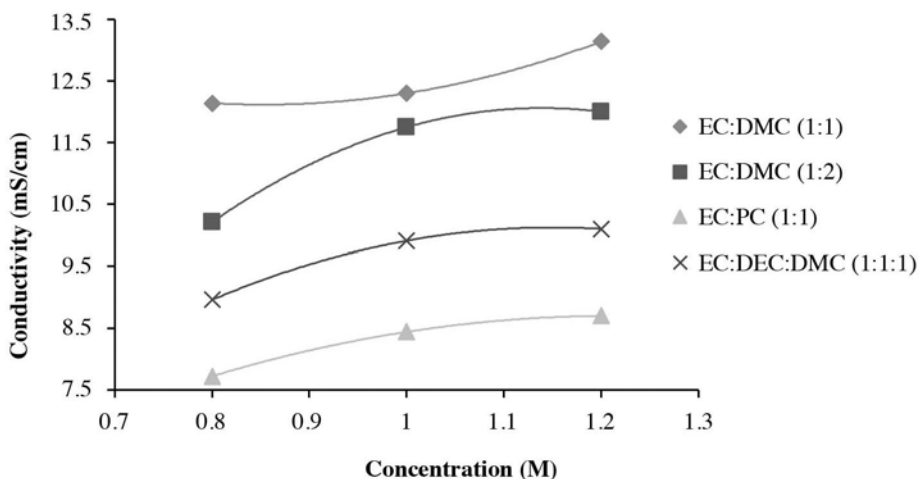
Figure 1. *Ionic conductivity of NaPF$_6$ electrolytes based on binary and ternary systems of organic solvent at various concentration*

Electrochemical Window Stability

Figures 2 show the electrochemical window stability of 1.0 M NaPF6 in EC:DMC (1:1) with the mixture consisting of preheated materials and non-heated materials, respectively. Based on Figure 2, the operating window voltage of preheated 1.0 M NaPF6 in EC:DMC (1:1) electrolyte were observed as stable after a first few runs. Nevertheless, the electrolyte is stable up to 3.5 V without forming any electrochemical reactions.
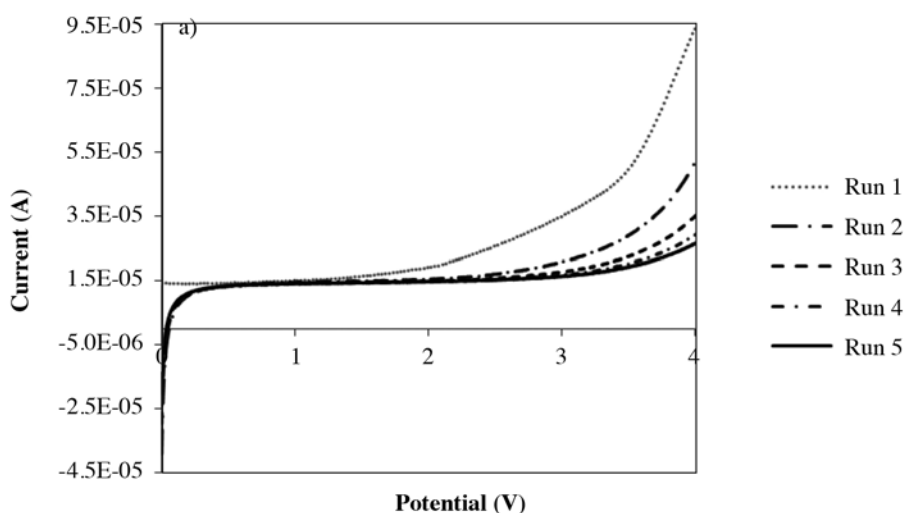

Figure 2. *Linear sweep voltammetry graph of 1.0 M NaPF$_6$ in EC:DMC (1:1) with preheated materials*

On the other hand in Figure 3, it was observed that some electrochemical reaction was occurring at the voltage window of 2.38 V to 3.33 V. This is due to the electrochemical reaction at the electrode surface, which was indicated by sudden increased of electron transfer between electrodes inside the glass bottle. However, for the 3rd run onwards, the electrolyte was stable up to 3.5 V. This show the existence of contaminants or undesired materials in the electrolyte, which was completely expelled, possibly in gaseous form after the 3rd run.
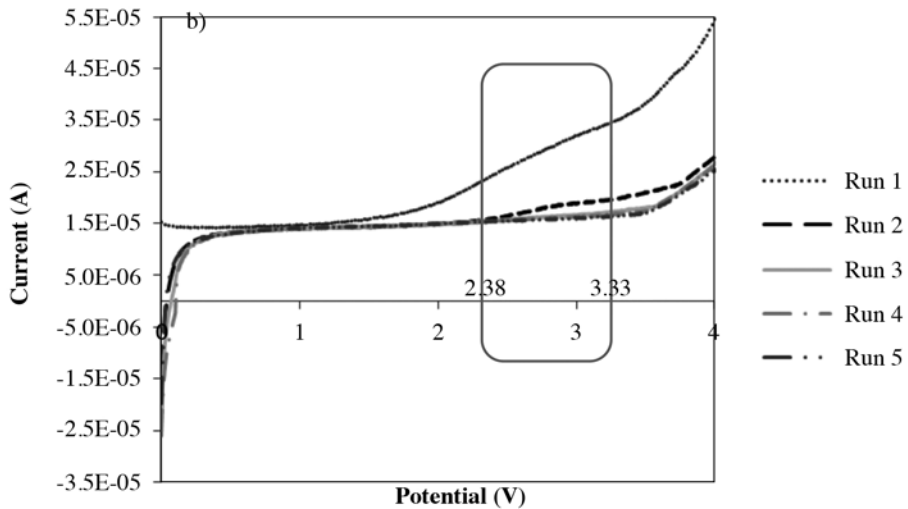

Figure 3. *Linear sweep voltammetry graph of 1.0 M NaPF$_6$ in EC:DMC (1:1) with non-heated materials*

Meanwhile in Figure 4, the behaviour of the mixture consisting preheated materials of 1.2 M NaPF$_6$ in EC:DMC (1:1) electrolyte were observed as stable up to 3.5 V after a first run onwards. This indicated that no contaminant was present in the electrolyte. It can be said that the contaminant or undesired materials present in the salt was effectively removed by preheating process.
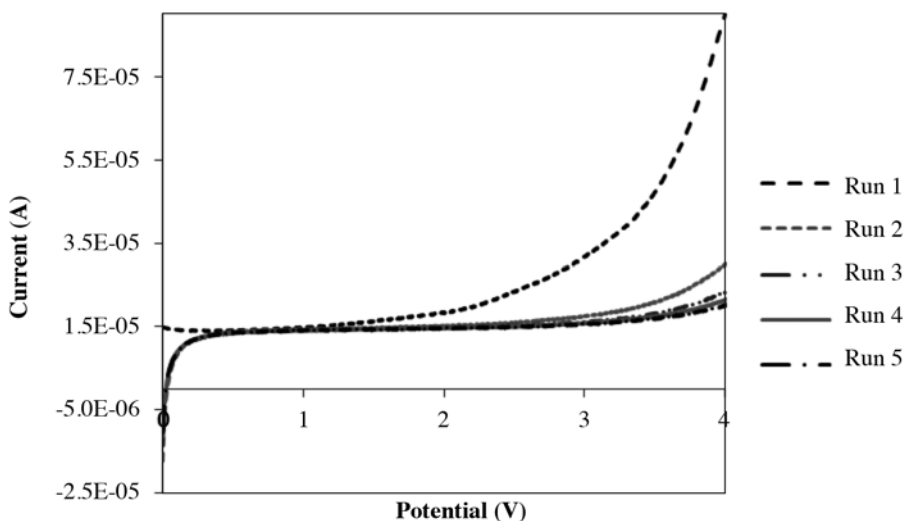
Figure 4. *Linear sweep voltammetry graph of preheated salt 1.2 M NaPF$_6$ in EC:DMC (1:1)*

Meanwhile in Figure 4, the behaviour of the mixture consisting of preheated materials of 1.2 M NaPF$_6$ in EC:DMC (1:1) electrolyte was observed as stable up to 3.5 V after the first run onwards. This indicated that no contaminant was present in the electrolyte. It can be said that the contaminant or undesired materials present in the salt was effectively removed by preheating process.

Discharge Capacity

Galvanostatic charge-discharge tests were carried out using the coin-type half cells with Na$_3$V$_2$PO$_4$ and sodium metal as cathode and anode respectively. Figure 5 indicates the discharge profile of Na/ Na$_3$V$_2$PO$_4$ cell using 1.0 M NaPF$_6$ in EC:DMC (1:1) electrolyte. Specific capacity at 93.99 mAhg^{-1} were recorded in 1st cycle and maintained at discharge capacity of 73.99 mAhg^{-1} at the 10th cycle.
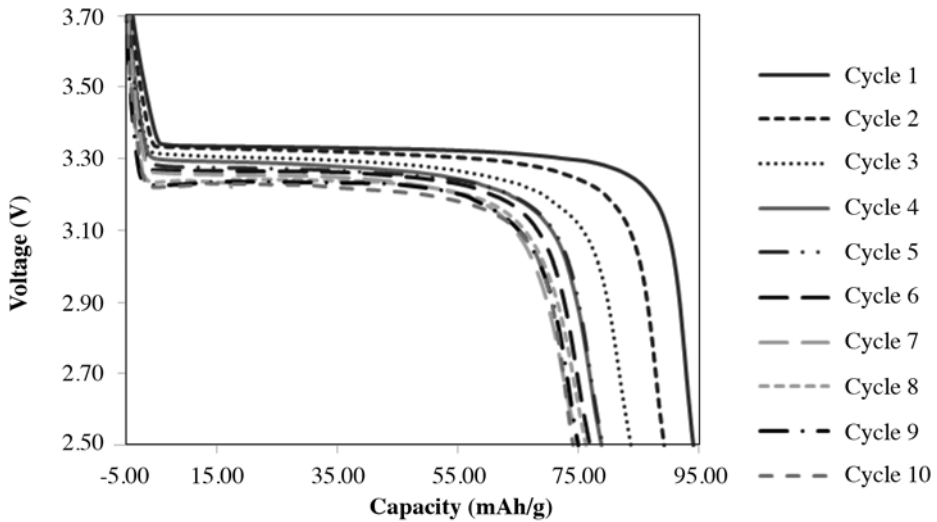
Figure 5. *Discharge capacity of cell using preheated 1.2 M NaPF$_6$ in EC:DMC (1:1)*

Figure 6 shows the discharge profile of preheated 1.2 M NaPF6 in EC:DMC (1:1) The highest discharge capacity of Na/ Na3V2PO4 cell rates of 1.2 M NaPF6 in EC:DMC (1:1) were recorded as 89.25 mAhg-1 obtained from the 1st cycle. However, the rate capability has gradually decreased upon increasing the cycle number, at which the lowest of 53.80 mAhg-1 obtained from the 10th cycle. Based on the galvanostatic charge-discharge measurement, the electrolyte of 1.0 M NaPF6 in EC:DMC (1:1) had produced better result where the discharge capacity was higher and can retain higher capacity upon repetitive cycling as compared to 1.2 M NaPF6 in EC:DMC (1:1).
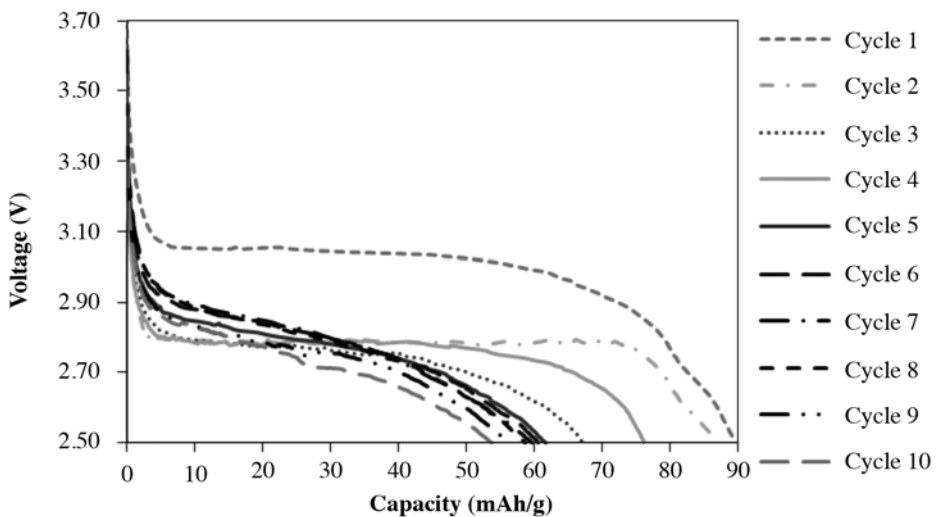

Figure 6. *Discharge capacity of cell using preheated 1.2 M NaPF$_6$ in EC:DMC (1:1*

CONCLUSION

The electrolyte materials for the binary system consisting of 1.2 M $NaPF_6$ in EC and DMC (1:1) had resulted in the highest ionic conductivity at 13.14 mS/cm, followed by 1.0 M $NaPF_6$ in EC:DMC (1:1) at 12.30 mS/cm. Meanwhile, binary system of 0.8 M $NaPF_6$ in EC and PC (1:1) had lowest ionic conductivity at 7.72 mS/cm. The operating window voltage of preheated 1.0 M $NaPF_6$ in EC:DMC (1:1) electrolyte were observed as more stable after a first few runs than non-heated 1.0 M $NaPF_6$ in EC:DMC (1:1) electrolyte where electrochemical reaction was observed at voltage of 2.38 V to 3.33 V. All electrolytes showed a stable electrochemical window stability of up to 3.5 V. The preheat materials were very essential in providing good stability as unwanted contamination were eliminated during the process. The highest capacity of 93.99 mAhg^{-1} were obtained from 1.0 M $NaPF_6$ in EC and DMC (1:1), while the capacity of 89.25 mAhg^{-1} were obtained using 1.2 M $NaPF_6$ in EC and DMC (1:1). The 1.0 M $NaPF_6$ in EC and DMC (1:1) electrolyte had displayed an excellent ionic conductivity and discharge capacity.

ACKNOWLEDGEMENT

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