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Investigation the Effect of DMMP as Electrolyte Additive on the Flammability and Electrochemical Properties of Lithium-Ion Batteries

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Abstract- Dimethyl methyl Phosphonate (DMMP) was used as a flame retardant to reduce the flammability of the electrolyte with minimum negative impact on the electrochemical performance of the electrodes. The flammability and thermal stability of prepared electrolyte in the presence of DMMP by different contents were evaluated using self-extinguishing time (SET), differential scanning calorimeter (DSC). Linear Sweep voltammetry (LSV) and galvanostatic charge and discharge tests were carried out to investigate the effect of DMMP on the electrochemical properties. When a sample containing 5 vol.% DMMP is used as electrolyte in 18650 cell, the cell exhibits quite good cycling stability; like the Blank electrolyte with capacity fade after 55 cycles at 0.1 C is 92.68 and 96.59%, respectively. The cathode electrode interface is characterized with EIS, SEM, and XRD, DSC after several charge/discharge cycles which demonstrate stable and liner protective film is formed on the surface of cathodes in the presence of 5 vol.% DMMP. The results imply that DMMP is a promising option as highly flame-retardant and electrochemically compatible electrolyte additive for safe lithium-ion batteries.

Keywords- Thermal stability, CEI layer, 18650 cells, Lithium-Ion Batteries, Flame retardant, DMMP, Dimethyl methyl phosphonate

1. INTRODUCTION

Lithium-Ion Batteries (LIBs) are attractive candidates as a power source in hybrid and electric vehicles due to their high specific energy, large energy density and good cycling stability. Safety concern of lithium ion batteries, in the recent years, have been the key problem in their practical applications because organic solvents which are used in their electrolyte component such as Ethylene carbonate (EC) Dimethyl carbonate (DMC) Diethyl carbonate (DEC) Ethyl methyl carbonate (EMC) are very flammable and can be ignited in the situations of various types of accidents and abuses, which has imparted the state-of-the-art electrolyte systems with potential fire hazards [1-3]. The efforts aiming to improve the thermal stability of electrolytes have been intensified in the recent years, especially driven by the more stringent safety requirements for large industry lithium-ion batteries intended for electric vehicles. The most efficient and economical ways use flame retardants (FRs) as electrolyte additives or co-solvents [4,5]. The performance and stability of the electrolyte are highly dependent on the presence of impurities such as chlorine, water and HF. It is well known that large amounts of hydrofluoric acid (HF) are produced at elevated temperatures due to the thermal decomposition of $LiPF_6$ based carbonate electrolytes initiated by trace impurities of water as shown in Scheme 1.

$LiPF_6 \leftrightarrow LiF + PF_5$

$PF_5 + H_2O \rightarrow OPF_3 + 2HF$

$OPF_3 + 2xLi^+ + 2xe^- \rightarrow Li_xPF_{3-x}O + xLiF$

$OPF_3 + 3H_2O \rightarrow PO_4H_3 + 3HF$

Scheme 1 The auto-catalytic thermal decomposition of $LiPF_6$-based carbonate electrolytes [6,7].

The cyclability of rechargeable LIBs also greatly depends on the structural properties of the electrode materials during charging and discharging processes. Phosphonate-based compounds were previously reported as flame-retardant additives for lithium ion battery owing to the ability of radical scavenging for the combustion reactions and char formation in gas phase. In addition, Dimethyl methyl phosphonate flame retardant can be regarded as a compound forming CEI layer upon the surface of the cathode electrode, which depends on oxidation potential.

Initial investigations on flame retarding additives for application in lithium-ion batteries have focused on organophosphorus compounds, in particular, such as trimethyl phosphate [8], triethyl phosphate [9], trimethyl phosphite [10], and cyclo-phosphazenes such as hexa-methoxy-cyclo-phosphazene (HMPN) [9-11] and Bis (2,2,2-Trifluoroethyl) Ethyl-phosphonate [12]. dimethyl(2-methoxyethoxy) methyl-phosphonate (DMMEMP) [13]. and dimethyl methyl-phosphonate (DMMP) [3,14-16]. Phosphonate compounds are known as FRs that function in the vapor phase by a radical mechanism. Since the high content of flame retardants in many cases reduce the cells performance, it is important to optimize the additives content in the electrolyte of LIBs. The objectives of this work are to investigate the effect of DMMP electrolyte additive on the flammability, thermal stability and electrochemical performance in the 18650 commercial cells. To the best of our knowledge DMMP is reported as flame-retardant and CEI forming on the surface of cathode material in lithium ion batteries with highly flame retardant and good electrochemical performance for the first time. Therefore, DMMP is a promising Flame-Retardant additive that has recently garnered researchers' attention.

2. EXPERIMENTAL

The flammability tests of the electrolytes without and with DMMP additive by Self-extinguishing time (SET) were performed. An asbestos-fiber fiberglass sheets (~5 cm in length, ~2 cm in width) were immersed in the as prepared electrolyte to absorb about 0.2 g electrolytes then it was ignited to evaluate the flammability of the prepared electrolytes [16]. The time for the flame to extinguish was recorded 5 times for each sample. The thermal stability of the electrolytes was determined by means of differential scanning calorimeter (DSC) at a heating rate of 5 °C min^{-1}, in the temperature range from 25 to 300 °C. The DSC measurements were performed using a DSC6200 instrument.

The electrochemical experiments were carried out using Li metal and anode active material NMC as electrodes and 18650 cells. 1 M $LiPF_6$ in EC: DMC 1:1 by volume as electrolyte and micro-pores polypropylene membrane as separator. The composite electrode used for electrochemical measurements were prepared by mixing the active materials, acetylene black, and polyvinylidene fluoride (PVDF) binder in weight ratio of 85:8:7 using N-methyl-2-pyrrolidone (NMP) as solvent. The obtained slurry was then cast onto aluminum foil, and then dried at 120 °C in a vacuum drying oven for 12 h. The cells were assembled in an argon-filled glove box with moisture and oxygen levels less than 10 ppm and tested by galvanostatic charge-discharge cycling between 2.3 and 4.3 V using (New ARC V/10 mA, China) battery tester. The Linear sweep voltammetry (LSV) between 3 V -6 V *vs.* Li/Li^+, scan rate 0.5 mv/s and electrochemical impedance spectroscopy (EIS) test in the frequency range of 0.01–100 kHz and an AC potential as amplitude voltage of 5mV was performed with a Galvanostat/Potentiostat Autolab (PGSTAT 302N). To analyze the composition and microstructure of the electrodes after charge–discharge cycling measurements, the cells were disassembled in an argon-filled glove box. The NMC electrodes were then washed with anhydrous dimethyl carbonate (DMC) 1 mL for three times to remove residual $LiPF_6$ and EC, followed by vacuum drying overnight at room temperature [17]. The surface morphology of the electrodes was observed by scanning electron microscope (SEM, JEOL JSM-7001F/SHL, JEOL Inc). The phase structure of surface layer on the cathode was measured by X-ray diffraction (XRD, Rint- 2000, Rigaku) using Cu Kα radiation in an angular range of 10-70° (2θ). The thermal stability of the electrode was determined by DSC at a heating rate of 10 °C min^{-1}, in the temperature range from 25 to 200 °C.

3. RESULTS AND DISCUSSION

The results of the electrolyte flammability tests are shown in Fig. 1. It can be seen from Fig. 1(a) that the Blank electrolyte is very flammable and causes to flare followed by an explosion [18]. It should be noted that the self-extinguishing time (SET) curves of electrolyte with 5 vol.% DMMP show a sharp decrease which indicates a very good anti-flammability effect of DMMP additive. When the DMMP additive content reaches about 40 vol.%, the electrolyte becomes completely non-flammable (SET=0 s g^{-1}) and cannot be ignited which shown in Fig. 1 (b) and Fig. 1 (c). When DMMP as a flame retardant (FR) is added in the electrolyte, the burning time decreases and hence the flammability drops. In general, organo-phosphorus compounds are known as flame-retardants that can function in the vapor phase by a radical mechanism. Usually the phosphorus content of this kind of flame-retardants can reflect the efficiency of flame retarding. DMMP has higher phosphorus content than the previous investigated FRs additives. Therefore, DMMP can be used as a flame-retardant (even totally nonflammable) additive in a non-aqueous electrolyte for application in Li-Ion batteries' electrolyte [3].

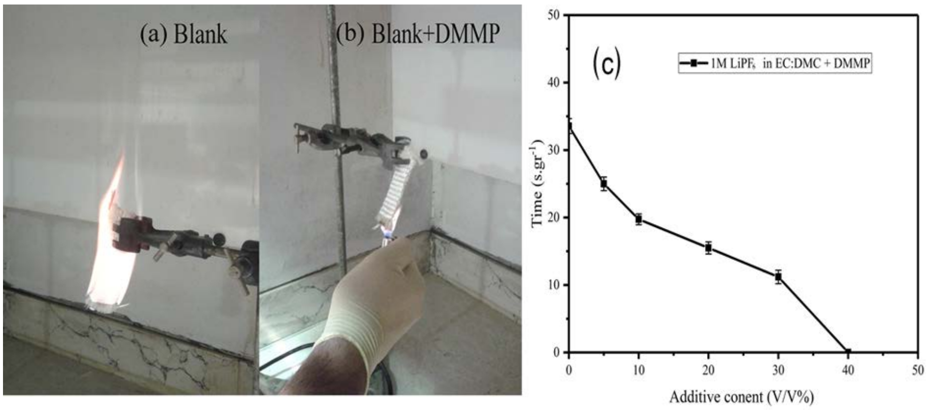

Fig. 1. The view of flammability test for electrolyte with DMMP (a); without DMMP (b) and results of SET tests of the electrolytes containing different concentration of DMMP with error bar (c)

The DSC scans of the Baseline electrolyte with and without DMMP additive are given in Fig. 2. Three endothermic peaks are observed at about 110 °C, 175 °C and 185 °C in the electrolyte without FR. DMMP-containing electrolytes display one peak at about 198 °C. The thermal stability of Li-ion cells is improved by using DMMP-containing electrolytes. DMMP contains P as a flame-retardant element, which improves the reaction temperature of the electrolytes [19].

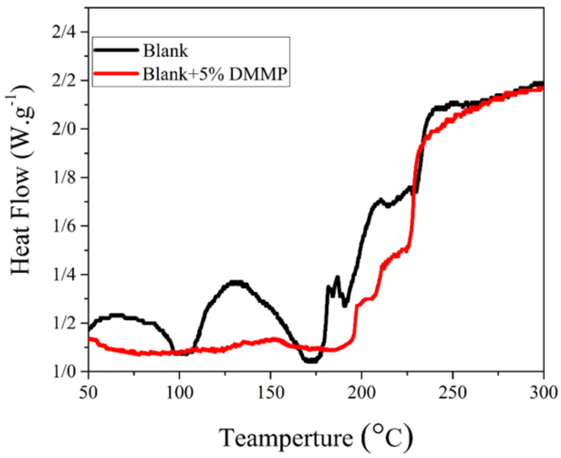

Fig. 2. DSC profiles of the two electrolytes: Blank electrolyte (Black Line) and Blank electrolyte +5% vol of DMMP (Red Line)

In Fig. 3 is shown the Linear Sweep voltammetry graphs of two samples, Blank electrolyte and electrolyte containing 5 vol.% of the DMMP additive. As it can be seen the electrolyte which has 5 vol.% of additives oxidized earlier than the Blank sample, during the oxidation sweep seen in Fig. 3, there was a small oxidation peak around 4.1 V *vs*. Li/Li^+ for DMMP 5 vol.%, which was not observed in the Blank electrolyte [20]. While the oxidation peak around 4.4 V *vs*. Li/Li^+ is assigned to the oxidation of Ethylene Carbonate. Due to the earlier oxidation of the electrolyte with a DMMP additive, it can be expected that on the surface of the cathode electrode, during the charge process, a layer formed by additive decomposition, which is known as the CEI layer.

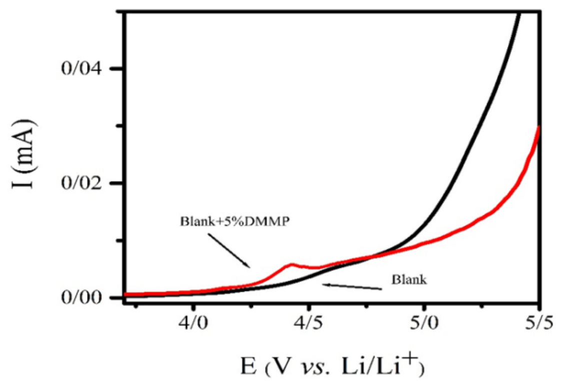

Fig. 3. Linear sweep voltammograms of 1 M $LiPF_6$ EC/DMC (1/1, v/v) solutions without and with 5 vol.% of additives. Pt as the working electrode and Li as the reference and counter electrode. Scan rate is 10 mV s^{-1}

The electrochemical properties of the NMC/graphite full cell with Baseline electrolyte and Baseline electrolyte +5 vol.% DMMP were investigated using coin-type cells. The first discharge/charge cycles were tested at 0.1 C rate, and the corresponding initial discharge/charge curves are shown in Fig. 4 (a). The galvanostatic charge/discharge capacities of the NMC cathode in the Baseline electrolyte and electrolyte containing 5, 7, 10, and 20 vol.% are 2182, 2159, 2166, 1891 and 1784 mAh, respectively. The charge/discharge profile demonstrated that the electrolyte by 20 vol.% of DMMP can make the electrolyte be hardly flammable, exhibiting high-efficiency flame retardant, in the contrary, the 20 vol.% DMMP-containing electrolyte has shown lower electrochemical properties compared to other samples and it cause to reduce the capacity to 1784 mAh. Therefore, the amount of additive cannot be chosen more than 10 vol.% the higher content of additives may lead to increase the viscosity of obtained electrolyte as a result of which the ionic conductivity of electrolyte would be decreased. It is indisputable that prepared batteries using more than 10 vol.% of additives should show lower practical capacity and electrochemical performance compared to samples with lower content of additives. The cycle life of 18650 cells with Blank electrolytes, 5 and 7 vol.% of DMMP containing electrolytes are shown in the Fig. 4 (b). The capacity retention of the electrolyte containing 5 vol.% of DMMP is about 92.68 % after 55 cycles which means it is almost equal to the Blank sample except it has higher thermal and flame stability. Compared to the Blank sample, the sample that has 7 vol.% of the additive, practical capacity drops to 77.72% of initial capacity, indicating that it is not appropriate to use as an electrolyte additive in lithium batteries. A decrease in the sample capacity of 5 vol.% of the additive compared to the control sample has a slight difference in comparison with the effect on reducing the flammability [16].

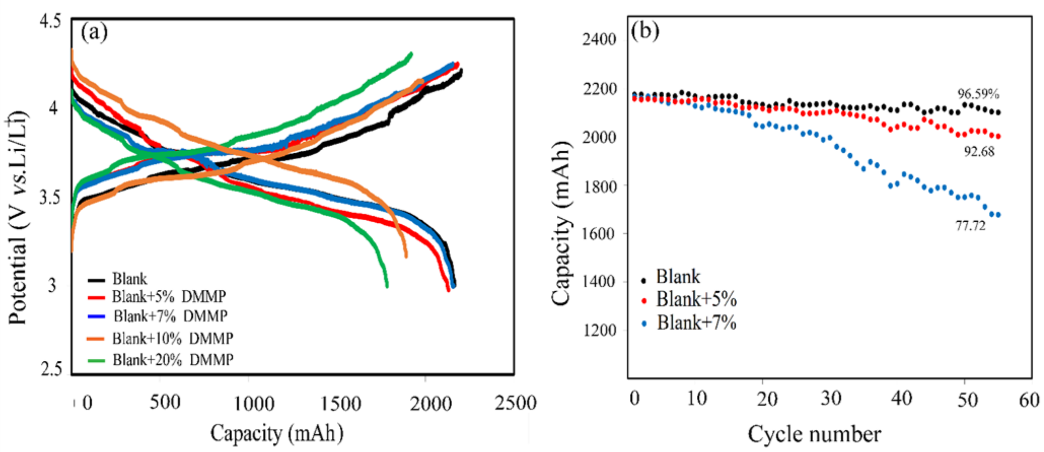

Fig. 4. Initial Charge/discharge curves of the cell with blank electrolyte and electrolyte containing different amount of DMMP additive (a) and cycling performance of 18650 cells with Blank electrolyte, Blank electerolyte+5% and Blank electerolyte+7% content of DMMP additive

In order to further understand the structural and interfacial behavior of the electrode/electrolyte, EIS measurements were conducted in the frequency range of 100 KHz to 10 MHz at the full charge state. Fig. 5 presents the Nyquist plots of the cells. The first point of contact with the horizontal axis indicates the resistance of the solution (R_s). The spectra typically consist of a semi-circle in the high frequency region related to charge transfer resistance (R_{ct}) and an inclined line at low frequency Warburg impedance (Z_w), which is associated with lithium-ion diffusion of the electrode [21].

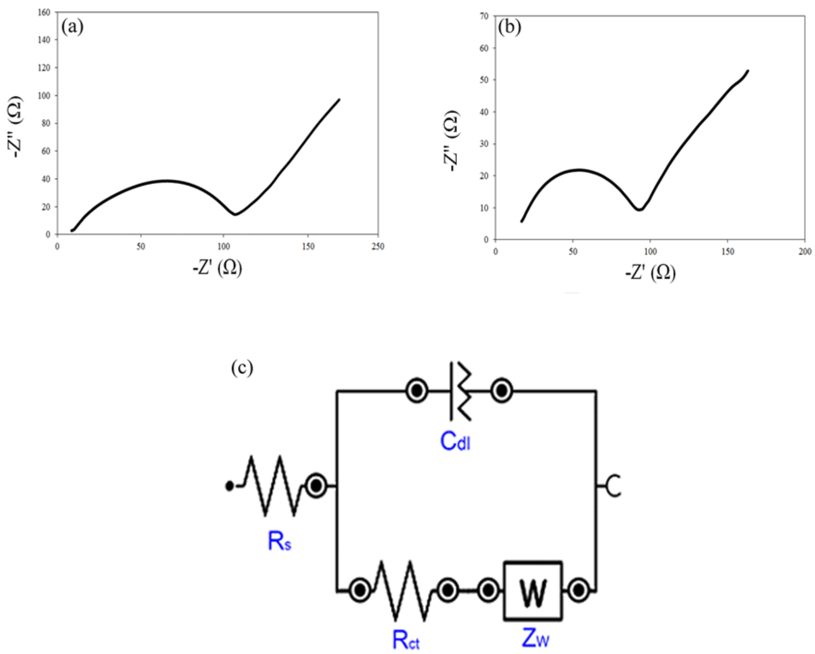

Fig. 5. Nyquist plot of half-cell with (a) Blank electrolyte; (b) Blank electrolyte +5 vol.% of DMMP additive and (c) equivalent circuit

The R_s for Blank electrolyte is about 11.09 ohm, which is less than the R_s for the electrolyte sample with the DMMP additive. According to the aforementioned reason the addition of DMMP additive to the prepared electrolyte samples leads to rise the viscosity of solution and decrease the ionic conductivity which means the higher additives content leads to higher R_s. The impedance data and the data for fitted plot are shown in Table 1. The equivalent circuit composed of capacitance and resistance has been monitored in Fig. 5(c).

Table 1. The data of Electrochemical Impedance Spectroscopy and fitting data

Sample	**R_s (Ω)**	**R_{ct} (Ω)**	**C_{dl} (μF)**
$LiFePO_4$/Li in Blank Electrolyte	11.09	109.29	145
$LiFePO_4$/Li in Blank Electrolyte+5% DMMP	16.75	92.58	167
$LiFePO_4$/Li in Blank Electrolyte (fitted)	12.58	135.88	151
$LiFePO_4$/Li in Blank Electrolyte+5% DMMP (fitted)	16.08	91.28	169

The charge-transfer resistance R_{ct} of Blank electrolyte and electrolyte containing DMMP are

109.29 and 92.58, respectively. DMMP cell exhibits smaller R_{ct}, indicating that electrons and Li^+ can transfer more quickly on the interface of active materials and electrolyte. The slope of the impedance of DMMP electrode in the low frequency region is bigger than that of Baseline electrolyte [22,23].

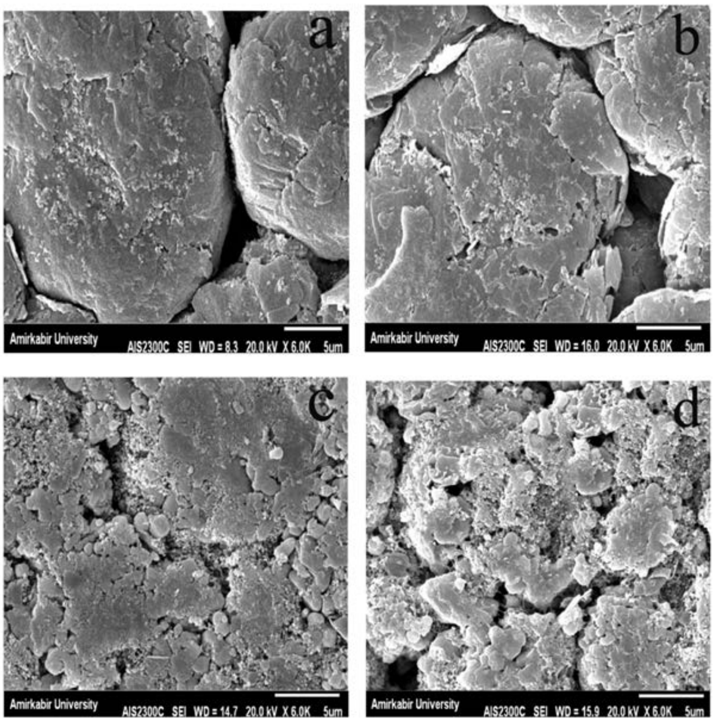

Fig. 6. SEM images of Graphite (a) and NMC (c) electrode cycled with electrolyte containing 5% of DMMP and Graphite (b) and NMC (d) electrode cycled with Blank electrolyte

From SEM results shown in Fig. 6, it can be found that the morphology of the Graphite electrode cycled with 5 vol.% DMMP shown in Fig. 6 (a) exhibit more uniform morphology compared with the Graphite electrode cycled with Blank electrolyte (see Fig. 6 (b)). It can be clearly seen that graphite electrode which is cycled in blank electrolyte shows deeper crack on the surface of its particle and some exfoliation around the edge of graphite particles in comparison with cycled electrode in electrolyte with additive. It can be attributed to the effect of SEI composed on the graphite's surface and its influence to exfoliation of graphite. As can be seen in Fig. 6 (c) and Fig. 6 (d), the surface of the electrode cycled with the Blank electrolyte, dotted by a non-uniform layer of electrolyte and salt decomposition products (see Fig. 6 (d)). These fine particles and impurities on the surface of the electrode result from the decomposition of lithium hexafluorophosphate salt and the early oxidation/reduction of ethylene carbonate. While the charged electrode surface with the electrolyte containing additive is completely clean and smooth, it prevents the oxidation/reduction of ethylene carbonate and forms a thin layer, reducing the resistance and protecting the surface of the electrode [10,20]. The results of the SEM are completely compatible with the results of the electrochemical impedance spectroscopy and linear sweep voltammetry tests.

The DSC analysis of the cycled NMC electrode by the Blank and containing 5 vol.% DMMP electrolytes are shown in Fig. 7. The NMC electrode charged by the Blank electrolyte exhibited 3 exothermic peaks about 110, 120 and 160 respectively, which is related to the destruction of $LiPF_6$ salt and carbonate solution. The increase in temperature causes the electrode to be degraded, resulting in heat release and rising temperatures inside the battery, increasing the risk of thermal runaway and explosion in the battery [16]. In Fig. 7 it is quite obvious that the electrode charged with electrolyte added 5 vol.% of the additive completely thermally stable and no degradation peak appears. The results show that the layer formed on the electrode surface by the electrolyte containing 5 vol.% DMMP has a high thermal stability and not degraded up to about 200 °C.

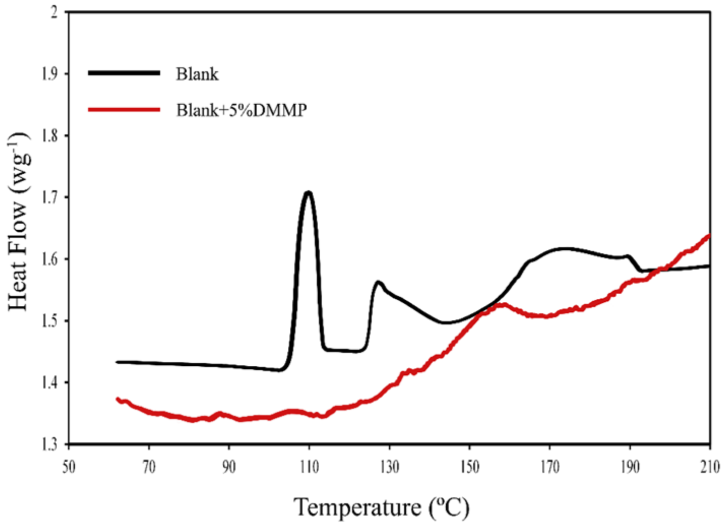

Fig. 7. DSC curves of the NMC electrode after cycling with the Blank electrolyte (Black Line) and Blank electrolyte+5 vol.% DMMP additive (Red Line)

The x-ray diffraction (XRD) patterns of the pristine NMC electrode and charged NMC electrode in the Blank electrolyte and electrolyte containing 5 vol.% DMMP are shown in Fig. 8. All XRD patterns have been analyzed with X'Pert software and all data were compatible to the NMC XRD pattern with standard code (ICDD PDF 56-0147). The patterns of NMC electrode that charged by electrolyte containing 5 vol.% DMMP is sharper than that of NMC charged by Blank electrolyte, indicating the high degree of crystallization of the cathode material [17]. However, the intensities of main diffraction peaks of cycled electrode with Blank electrolyte is broadened and weakened, which confirms that DMMP helps to preserve the crystallinity and the structural stability of the cycled NMC electrode due to the oxidation of the DMMP additive prior to the electrolyte and the formation of a protective layer on the electrode surface, it improves the crystallinity of the electrode, thereby facilitating the entry and exit of lithium ion into the electrode structure [24-26].

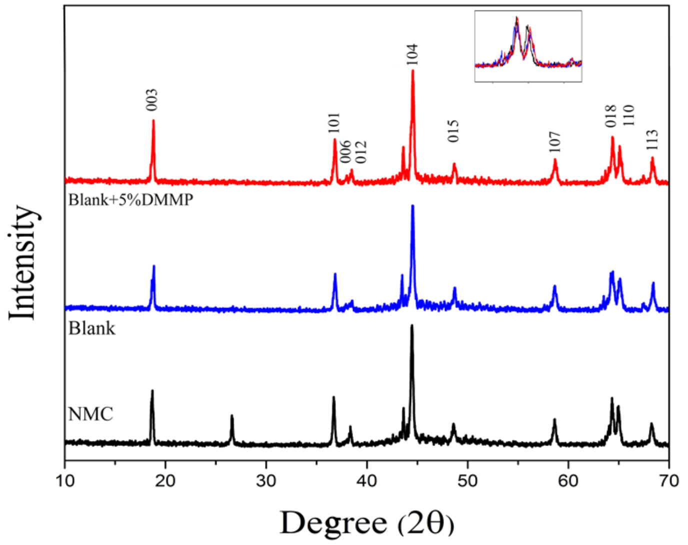

Fig. 8. XRD patterns of NMC electrode: prior to the test (Black Line), after cycling with Blank electrolyte (Blue Line) and cycling with Blank electrolyte +5 vol.% DMMP additive (Red Line)

4. CONCLUSION

We have shown that commercially available DMMP acts as a flame retarding additive for lithium-ion batteries and exhibits a good electrochemical performance, lower oxidation potential than that of EC, forming the CEI on the surface of cathode, high thermally stable, in addition it has an appropriate and economic price which make it an outstanding candidate for commercial batteries. However, the presence of DMMP narrows the electrochemical window of the electrolyte. The electrolyte containing 5 vol.% has a good thermal stability and acceptable electrochemical performance compare to the Blank electrolyte due to the formation of a protective layer on the surface of the electrode (CEI) and the convenience of lithium to the structure of the electrode.

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