ENABLING HIGH-VOLTAGEGRAPHITE/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ LITHIUM-ION FULL CELL

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ABSTRACT. The present works develops method to prepare high-voltage full coin cells, using graphite as the negative electrode and LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO) as positive electrode. Detailed instructions are provided to researchers enable to prepare their own high-quality full coin cell. Half-coin cells performed separately with graphite or LNMO were also made to provide the repeatable data and accurately predict how a material would perform in an actual lithium coin cell (referred to as "full-cell"). In addition, different electrolyte systems using carbonates-based solvents were investigated for electrode – electrolyte compatibility testing to choose the most appropriate electrolyte in further coin cell preparation. The full cell is expected to work at the potential of 4.7 V (vs Li$^+$/Li) and delivered a specific capacity of 120 mAh.g^{-1}.

KEYWORDS: *lithium-ion, full-cell, high-voltage, graphite, LiNi$_{0.5}$Mn$_{1.5}$O$_4$*

1. INTRODUCTION

Lithium-ion batteries (LIBs) have been widely used in a large variety of electronic applications since their commercial release in 1991, providing energy for everything from portable devices to electric vehicles [1]. To the present day, state-of-the art Li-ion coin cells essentially maintain the original configuration, employing a generation of LiCoO$_2$, i.e nickel-based LiNi$_{1-x}$M$_x$O$_2$ (M = Co and Mn/Al) as the cathode, and graphite as the anode could offer gravimetric energy densities up to around, respectively, 260 Wh.kg^{-1} and 780 Wh.L^{-1}, approaching the 300 driving mile range target for plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs) [2]. The demand for LIBs technology has been continuing to demonstrate high energy rechargeable lithium (Li) metal batteries up to 500 Wh.kg^{-1} for the future EVs generation.

Thus, the design of appropriate electrode systems is of prime importance to realize a high energy density (capacity x voltage) to perform other available system. Principally, the output voltage of a Li-ion cell is determined by the difference in electrochemical potential between the two electrode materials. To date, graphite is currently the most common anode used in LIBs while large-capacities negative electrode (e.g., silicon-based materials) is still in challenge for long-term cycling performance. Meanwhile, substantial research efforts from both academic and industrial communities have focused on the design of novel positive electrode materials with large capacities (e.g., ≥ 200 mAh.g^{-1}) and/or high voltage (e.g., ≥ 4 V vs Li$^+$/Li), the key factor in enhancing cell energy densities [3-9].

Notable potential cathode candidates include nickel-rich layered oxides (LiNi$_{1-x}$M$_x$O$_2$, M = Co, Mn and Al), lithium-rich layered oxides (Li$_{1+x}$M$_{1-x}$O$_2$, M = Ni, Co, Mn, etc.), high voltage spinel oxides (LiNi$_{0.5}$Mn$_{1.5}$O$_4$) and high-voltage polyanionic compounds (phosphates, silicates etc). LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO) offers only a moderate specific capacity but hold a great promise for high power application if stable electrolyte system could be found to withstand its high operating voltage (4.7 V vs Li/Li$^+$) [2]. Notably, the electrode – electrolyte compatibility becomes a pivotal issue in this field, hence an emphasis is placed on the electrolyte recipes/additives to prevent the unwanted interactions of various high voltage-cathode materials and electrolyte system under highly oxidizing conditions.

The aim of this work is to realize the high voltage full Li-ion in coin-cell type using graphite/LNMO configuration. Firstly, the half coin cells were prepared separately for graphite or LNMO to understand its electrochemical performance and accurately predict its behaviour in full-cell configuration. Additionally, different electrolytes were investigated for electrode-electrolyte compatibility in half-cell and finally could be chosen the most suitable one for further full-cell cycling.

2. EXPERIMENTAL

2.1. Electrolyte preparation

Electrolyte solutions(Li-battery grade)contained LiPF$_6$, LiBF$_4$(Sigma-Aldrich, 99.9 %) in a solvent mixture, by volume, of ethylene carbonate (EC, Sigma-Aldrich, 99 %, < 20 ppm H$_2$O) and diethyl carbonate (DMC, Sigma-Aldrich, 99 %, < 20 ppm H$_2$O), ethyl methyl carbonate (EMC, Sigma-Aldrich, 99%, < 20 ppm H$_2$O) and vinyl carbonate (VC, Sigma-Aldrich, 99%,< 20 ppm H$_2$O).

Different electrolytes were prepared and tested for half-cell using LNMO or graphite. The electrolyte composition is detailed in Table 1.

Table 1. Electrolytes composition used for half-cell testing.

Nº	Electrolyte formula
1	EC-DMC (1:1) + 1M LiPF$_6$
2	EC-EMC (3:7) + 1M LiBF$_4$
3	EC-EMC (1:1) + 1M LiPF$_6$
4	EC-DMC (1:2) + 1.5M LiPF$_6$
5	EC-EMC (3 :7) + 1.2M LiPF$_6$ + 1 %wt. VC

2.2. Coin cell preparation

Full-coin cells were made with LiNi$_{0.5}$Mn$_{1.5}$O$_4$ as positive electrode and graphite as the negative electrode. Composite LiNi$_{0.5}$Mn$_{1.5}$O$_4$electrode on Al foil contain active material (MTI Corp., USA, 80 %wt.) along with conductive carbon

and binder (Super P 7.5 %wt, graphite 7.5 %wt., PVDF 5 %wt.). The positive electrodes had a mass loading of 4 mg/cm^2 (50 – 60 µm thickness). Composite carbon electrodes on Cu current collectors comprise graphite (MTI Corp., 95 %wt.) along with super P carbon (0.95 %wt.), 2.3 % wt. CMC solution (2 %wt. in water, MTI Corp.) and SBR (25 %wt in water, MTI. Corp.).The graphite negative electrodes had a loading of 8 mg/cm^2(120 µm thickness).

The electrodes were punched in air and heated under vacuum overnight at 120°C before transferred into the glovebox for coin-cell assembling. The half-cell configuration includes200 µm thick lithium foil (ribbon, Sigma Aldrich) as anode, Celgard separator (PE or PP) and graphite (or LNMO) as cathode. In order to keep the ratio of the electrolyte solution to electrode surface area constant, the same volume of electrolyte was used for all coin cells (80 µl). Figure 1 shows the construction design of full-coin cells that offer good precision for Li metal half cells [10]. Cell construction, spacer selection, etc. are described previously[11,12]. The full-cell graphite/LNMO was designed in capacity of 1.5 mAh within the anode to cathode capacity ratio controlled at 1:1.5.

All cells were cycled in temperature-controlled boxes (30.0^{o}C) between 3.5 – 4.85 V for half-cell and full-cell as well using battery testing device 16-channel MPG-2 (Biologic, France). Half-cell were cycled with C/10 rate at room temperature. The full-cell was first charged to 4.85 V by a constant current 0.1 C rate (CC mode) following by a constant voltage step at E = 4.85 V until the current decreased to 10% of applied charging current (CV mode), then the cell was cycled at rate C/10 for the next discharged and following cycles.

3. RESULTS AND DISCUSSION

The first step of this work was to build coin cells following conventional Li metal half-cell design. When preparing conventional half-cell, a piece of Li metal foil is used as the negative. The Li foil disk is usually larger than working negative of positive electrode.

3.1 Half-cell using Graphite electrode

The Li/graphite cells were cycled using a C/10 rate, lithiated fully at 0.005 V, then fully delithiated at 1.5 V. The important parameters, as defined on the first charge – discharge curve (Figure 2a, c, e), the plateau in the discharge curve at about 0.0.75, which is clearly ascribed to electrolyte reduction and formation of solid electrolyte interface (SEI) film [13,14].When SEI layer formed, itprevents the electrode from providing electrons to bulk electrolyte, thus terminating the electrolyte from continuous decomposition, thus stabilize the cycling performance of battery. Besides, the formation of SEI resulted in irreversible capacity about 50 mAh/g in various electrolyte compositions, induced unusual extension of coulombic efficient above 100%.In different electrolytes, the structure, morphology, thickness and composition of SEI layer could be changed which is resulted in the different in irreversible discharge capacity of first cycle [15,16]. The 1st discharge capacity of Li/C graphite cell was about 256; 325 and 290 mAh.g^{-1} in 1M LiPF$_6$ EC:DMC = 1:1; 1.5 M LiPF$_6$/EC:DMC = 1:2 and 1M LiBF$_4$EC:EMC=3:7 (Figure 2a, c, e) while expected theoretical capacity is about 340 mAh.g^{-1}. Although the discharge capacity in 1M LiPF$_6$EC-DMC= 1:1 is the lowest, the cycling behaviour is almost stabilized after 5 cycles without significant fluctuation. It

should be noticed that SEI layeralso dissolved and restructured during cycling, therefore the long-term cycling is challenged to achieve in some cases.For example, the electrolytes with percentage of high carbonate solvent (EC: DMC = 1:1, EC:EMC = 3:7) display an abrupt decrease of capacity about 100 mAh/g after 5-7 cycles. Many literature studies have reported electrolyte additives such as FEC and VC being known to improve cycle life and calendar life of Li-ion batteries [17-20]. Figure2g shows even high discharge capacity and excellent stable cycling and coulombic efficiency of Li/graphite cell in the electrolyte of 1.2M LiPF$_6$ EC:EMC = 3:7 + 1 %wt. VC. It is evident that additive VC improves the stabilization of SEI layer and enhances the cycling performance of half-cell. The reduction of less reduction stability VC avoids loss of electrolyte and form more stable and permeable SEI film [21].

3.2 Half-cell using LNMO electrode

Electrochemical charge and discharge of Li/LNMO cells were performed in the potential range of 3.5- 4.85 V (vs Li$^+$/Li) with C/10 rate. The plateau at ~ 4.7 V arises from the Ni$^{2+/4+}$ redox couple while the plateau at ~ 4.0 V is the result of Mn$^{3+/4+}$ couple. Due to the high voltage plateau, the electrolyte decomposition might be easily happened. To date, no electrolyte systems at the commercial stage can withstand its high operating potential (~ 4.7 V vs Li/Li$^+$), and issues including electrode – electrolyte parasitic reaction. Unexpectedly, CEI (cathode electrolyte interphase) couldn't be formed or functioned as effectively as SEI on anode side. Therefore, we could observe in Figure 3, the irreversible charge capacity of 1st cycle was eventually related to the decomposition of electrolyte in case of 1M LiPF$_6$ EC: DMC = 1:1; 1.5M LiPF$_6$ EC-DMC = 1:2; 1M LiPF$_6$ EC: EMC = 1:1; these values were 220 mAh.g^{-1}; 500 mAh.g^{-1} and 210 mAh.g^{-1}, respectively. However, in electrolyte of 1M LiBF$_4$ EC: EMC = 3:7, the 1st charge capacity is quite adequate, about 160 mAh.g^{-1} and the discharge capacity reach expectedly to theoretical value (138 mAh.g^{-1}). It means that this electrolyte is quite stable and CEI could be formed and grown up slowly during cycling to protect cathode surface and prevent the continuous electrolyte decomposition in further. After 50 cycles, the discharge capacity was still maintained at 125 mAh.g^{-1} and 115 mAh.g^{-1} for the cells using electrolyte of 1M LiPF$_6$ EC: DMC = 1:1 and 1M LiBF$_4$ EC: EMC =3:7. These cells have good coulombic efficiency (> 90%) but lose about 15 % of the initial value after 50 cycles. In contrary, the capacity fade is much worse for Li/LNMO cell with 1.5M LiPF$_6$ EC-DMC = 1:2; 1M LiPF$_6$ EC: EMC = 1:1. It is assumed that the stable performance could be only obtained with the proper electrode – electrolyte combination or the good compatibility between them. Otherwise, the incorporation of electrolyte additives has been found to be effectively passivate the composite electrodes. Herein, VC was also used as additive for Li/LNMO cell. Typical charge – discharge of cell using 1.2M LiPF$_6$ EC-EMC = 3 :7 + 1 %wt. VC showed that the low irreversible charge capacity and excellent stable capacity during cycling. Thus, the LNMO cathode performance was also improved with VC additive.

3.3 Full cell of Graphite/LNMO

The electrochemical cycling data of half-cell Li/Graphite and Li/LNMO was considering and optimizing to make the full-cell configuration. Otherwise, the initial design and

assembly method was the same as for half-coin cells. Many repeated full-coin cells were made and taken in prolonged cycling test in order to determine the reproducibility. The electrolyte 1.2M LiBF$_4$ EC-EMC = 3:7 + 1 %wt. VC was selected for long-term cycling due to the good compatibility with anode and cathode materials. Graphite/LNMO cell was slowly charged at rates 0.1C up to 4.85 V and kept at this voltage for fully charging. In Figure 4a, the initial charge curve showed a parasitic decomposition of electrolyte at fully charge state 4.85 V which was also reported in the study of Lu et al. [22]. Thus, prolong the fully charge state make severely decomposition of electrolyte. However, when the CV charge is long (> 6h), the discharge capacity is much greater (delivery more than 70% of the initial capacity), especially in high temperature cycling [22]. It was assumed that most of the initial capacity of LNMO can be recovered by extending the CV charge time [22]. In our case, at the room temperature cycling, the fade capacity was observed after 2 cycles (the initial value of 95 mAh.g^{-1}). After 50 cycles, the discharge capacity was only about 34 mAh.g^{-1} (remained 36% of initial capacity). It means that the CV charge time could be shortened to prevent vigorous decomposition of electrolyte leading to formation of thick and ineffective SEI layer; therefore, that could penalize unexpectedly the battery cycling performance. Indeed, further study will be performed to optimize the CV charge constant time and the stage of charge potential in order to achieve good capacity and cycling performance.

4. CONCLUSIONS

This work demonstrates methods for the construction of full Graphite/LNMO coin cells. In half-cell configuration, Li/Graphite or Li/LNMO cell exhibited the best cycling performance in electrolyte 1.2M LiPF$_6$ EC: EMC = 3:7 + 1 %wt. VC. It could be believed that VC additive is essential for forming a stable SEI on anode and cathode in order to achieve a long-term cycling. Thus, this electrolyte was selected for using in full-cell testing. In Graphite/LNMO full cell, the discharge capacity decreased dramatically upon cycling. The reason might be explained by the long-time of CV charge leading to the vigorous decomposition of electrolyte. Once the parasitic reactions were pronounced, the battery cycling performance could be consequently slowed down. Further studies will be performed on the optimization of charge state conditions to obtain stable cycling behaviour.
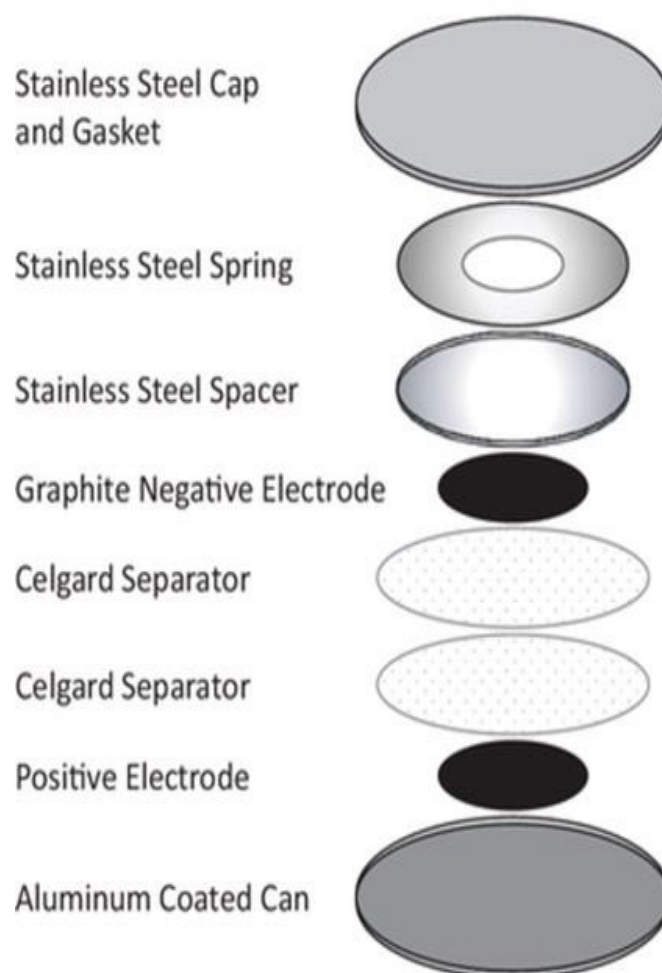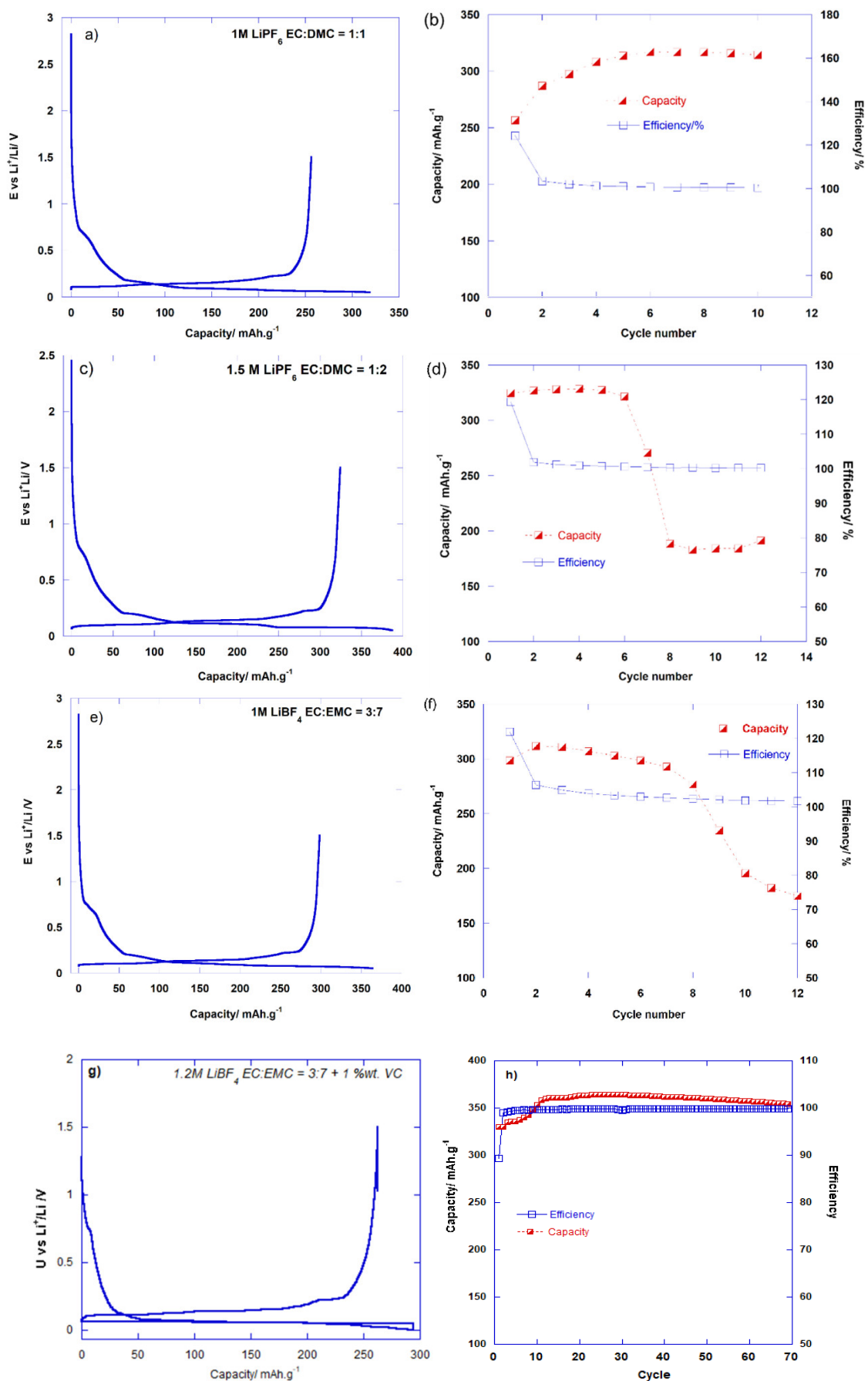

Figure 1. Diagram of Full Cell design. [10]

Figure 2. *1st Charge – discharge curves and cycling performance of Li/Graphite cells in different electrolytes: a-b) 1M LiPF$_6$ EC-DMC = 1:1; c-d) 1.5M LiPF$_6$ EC-DMC = 1:2; e-f) 1M LiBF$_4$ EC: EMC = 3:7; g-h) 1.2M LiPF$_6$ EC-EMC = 3:7 + 1 %wt. VC.*
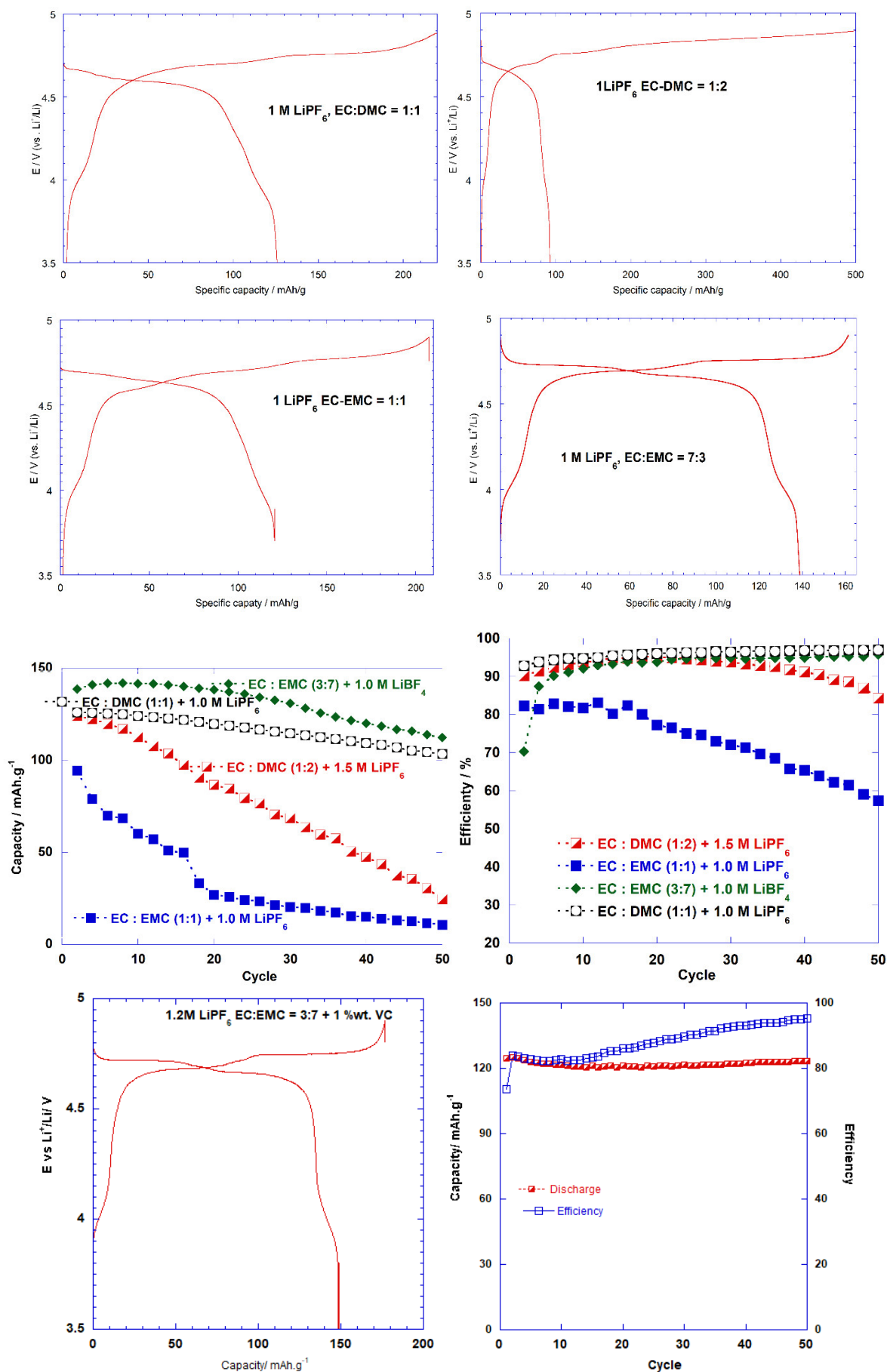
Figure 3. *1st Charge – discharge curves and cycling performance (discharge capacity and efficiency) of Li/LNMO cells in different electrolytes: 1M LiPF₆ EC-DMC = 1:1; 1.5M LiPF₆ EC-DMC = 1:2; 1M LiPF₆ EC-EMC = 1:1; 1M LiBF₄ EC:EMC = 3:7; 1.2M LiPF₆ EC-EMC = 3:7 + 1 %wt. VC.*
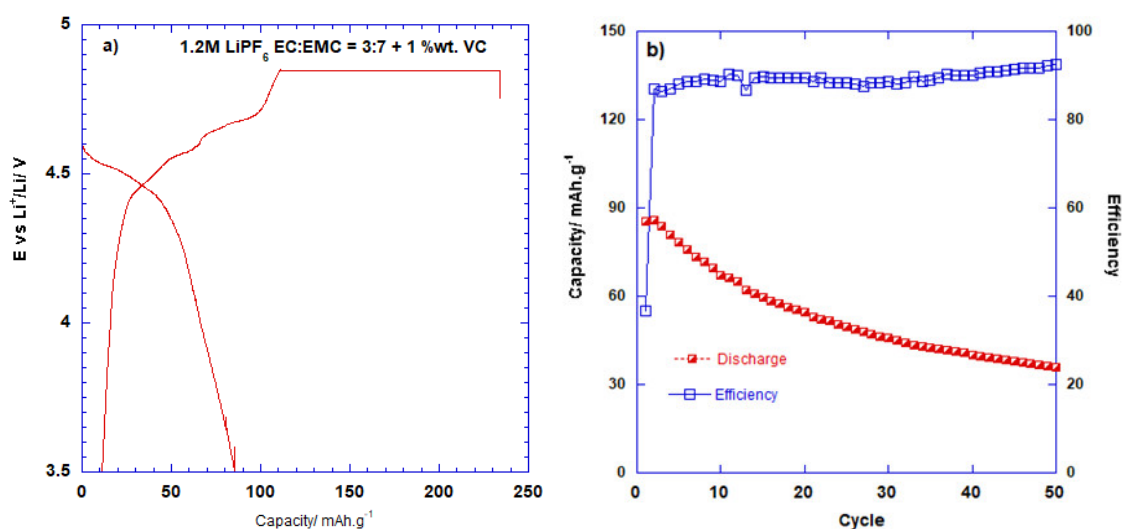
Figure 4. *1st Charge-discharge curve and cycling performance (discharge capacity and efficiency) of Graphite/LNMO full cell using electrolyte of 1.2M LiPF$_6$EC-EMC = 3:7 + 1 %wt. VC.*

5. ACKNOWLEDGMENTS

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