



## Short communication

## Electrochemical performance of nonflammable polymeric gel electrolyte containing triethylphosphate

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## ABSTRACT

Nonflammable polymeric gel electrolyte has been prepared by immobilizing 1 M  $\text{LiBF}_4/\text{EC} + \text{DEC} + \text{TEP}$  (55:25:20, v/v/v, EC: ethylene carbonate, DEC: diethyl carbonate and TEP: triethylphosphate) solution in poly(vinylidene fluoride-co-hexafluoro propylene) (PVdF-HFP) where TEP acts as a fire-retardant solvent in the gel electrolyte. The polymeric gel electrolyte has a high value of ionic conductivity of  $1.76 \text{ mS cm}^{-1}$  at  $28^\circ\text{C}$ . Thermal safety calorimetry (TSC) experiments show good thermal stability of the gel electrolyte. Cyclic voltammetry and charge/discharge cycling tests were performed on  $\text{LiMn}_2\text{O}_4/\text{gel}$  electrolyte and graphite/gel electrolyte half cells. The gel electrolyte works well for graphite/ $\text{LiMn}_2\text{O}_4$  cell although some improvement in the cycleability of the graphite electrode is still needed.

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## 1. Introduction

Safety issue is a major challenge in developing large size and high power lithium ion batteries (LIBs). Use of nonflammable electrolytes can solve this problem in LIB. To develop a safer LIB different approaches have so far been employed; for instance, use of solid polymer electrolytes, polymer electrolytes containing ionic liquids, or nonflammable solvents/co-solvents, etc. [1–10]. However, these approaches have their own disadvantages. That is, solid polymer electrolytes suffer from low ionic conductivity and inadequate electrolyte/electrode contact formation. Ionic liquids generally have low cathodic stability and poor charge–discharge cycle performances at graphite electrode [11–14]. Contrarily, polymeric gel electrolytes having sufficient nonflammability seems to be a good alternate to conventional electrolytes used in LIBs. This is because polymeric gel electrolytes show high ionic conductivity and good mechanical stability which are basic properties required to the electrolytes for practical LIBs.

Alkylphosphates, such as trimethylphosphate (TMP), dimethylmethylphosphate (DMMP), tributylphosphate (TBP), etc., have been examined as a co-solvent or an additive in the electrolytes to develop a nonflammable LIB system [8,15–17]. The addition of alkylphosphates reduces the flammability of the electrolytes but

the decomposition of alkyl phosphates on the anode (negative electrode) materials usually suppresses the  $\text{Li}^+$  insertion/desertion on the electrode [8,18]. To overcome this problem some additives viz. vinylencarbonate (VC), vinylethylenecarbonate (VEC), chloroethylene-carbonate (Cl-EC) were used as film forming agents of solid electrolyte interface (SEI) in the electrolytes [16,17,19]. We have previously reported a nonflammable polymeric gel electrolyte containing TMP as a fire-retardant co-solvent in the electrolyte with VC as an SEI film forming additive [20]. However, the addition of the film forming agents tends to deteriorate both the mechanical and thermal properties of the gel electrolyte.

In the present work, we have investigated a new fire-retardant co-solvent, triethylphosphate (TEP), in polymeric gel electrolytes. TEP itself shows the same nonflammable property as TMP, but is expected to have different electrochemical properties from TMP because of the differences in the alkyl groups. In this point of view, electrochemical tests were conducted for nonflammable gel electrolyte containing TEP with negative and positive electrodes. Improved electrochemical behavior of cathode (positive electrode:  $\text{LiMn}_2\text{O}_4$ ) and anode (negative electrode: graphite) with the gel electrolyte containing 1 M  $\text{LiBF}_4/\text{EC} + \text{DEC} + \text{TEP}$  has been observed without any additives to form SEI films.

## 2. Experimental

The component solvents, EC (Kishida Chemical; Battery grade), DEC (Kishida Chemical; Battery grade) and TEP (Wako Chemical)

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were used as received. The electrolytic salt,  $\text{LiBF}_4$  (Kishida Chemical), was also used as received, but kept in a glove box filled with dry Ar before use. A host polymer, PVdF-HFP (ARKEMA, Kynar 2851) was vacuum dried at  $100^\circ\text{C}$  prior to use and then stored in the glove box. The solution electrolyte was prepared by dissolving  $\text{LiBF}_4$  in a ternary solvent system of EC, DEC and TEP, where the mixing ratio of EC and DEC was kept constant, 2:1 (v/v). The polymeric gel electrolyte was prepared by a thermal casting method [21,22]. An appropriate amount of PVdF-HFP was dissolved in a mixed ternary solvent system (EC+DEC+TEP, typically 55:25:20, v/v/v) containing  $\text{LiBF}_4$ . The resulting mixture was stirred for 1 h to form homogeneous solution, and then poured on an Al pan. A transparent flexible film was obtained after heating the solution at  $110^\circ\text{C}$  for 13 min under reduced pressure (typically at 400 mmHg). This procedure was carried out in a dry Ar atmosphere.

The mass ratio of the solution component to the host polymer in the resulting gel was about 5:1, which was slightly dependent on the curing condition. The ionic conductivity of the gel electrolyte was measured by an ac impedance method in a frequency range from 100 kHz to 1 Hz using an impedance response analyzer controlled by a personal computer. Thermal safety analysis of the gel electrolytes was conducted by SYSTAG-Flexy TSC Safety Calorimeter in a temperature range of  $30\text{--}350^\circ\text{C}$  using a RADEX measuring cell. The test was carried out just in an open system like conventional DSC. The sample cell was assembled under a dry Ar atmosphere, but no gas was supplied during the measurements.

Cyclic voltammetry (CV) and charge/discharge cycling tests were performed using a conventional three-electrode cell with graphite (TIMREX KS6, TIMCAL) or  $\text{LiMn}_2\text{O}_4$  (Toda Kogyo) as the working electrode and Li foils as the counter and the reference electrodes. The graphite electrode was prepared from slurry containing the active material with 4 mass% of poly(vinylidene fluoride) (PVdF) binder and 1-methylpyrrolidine-2-on (NMP) solvent. On the other hand, the positive electrode was prepared by coating slurry containing 80 mass% of the active material  $\text{LiMn}_2\text{O}_4$ , 10 mass% of acetylene black, 10 mass% of PVdF and NMP as the solvent.

### 3. Results and discussion

Fig. 1 shows the temperature dependence of ionic conductivity of polymeric gel electrolyte containing 1.0 M  $\text{LiBF}_4/\text{EC} + \text{DEC} + \text{TEP}$

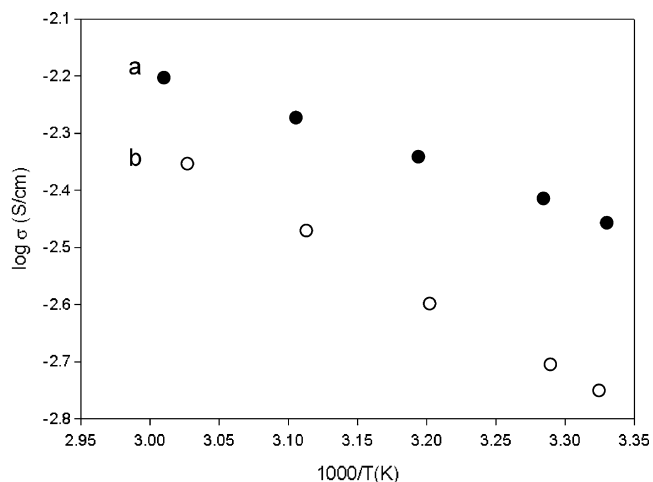


Fig. 1. Dependence of the ionic conductivity on temperature for (a) 1.0 M  $\text{LiBF}_4/\text{EC} + \text{DEC} + \text{TEP}$  (55:25:20) solution, and (b) 1.0 M  $\text{LiBF}_4/\text{EC} + \text{DEC} + \text{TEP}$  (55:25:20) gel.

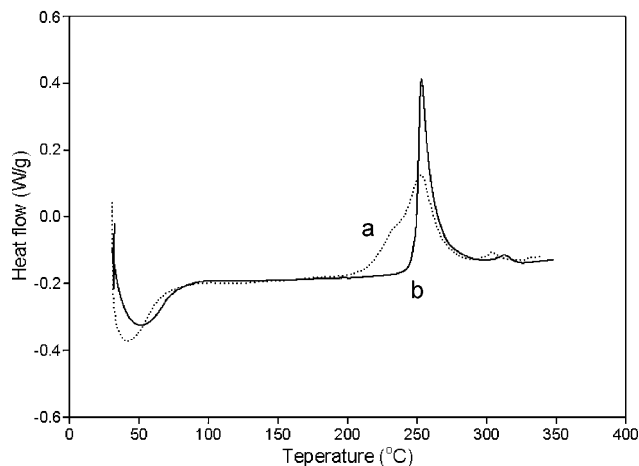
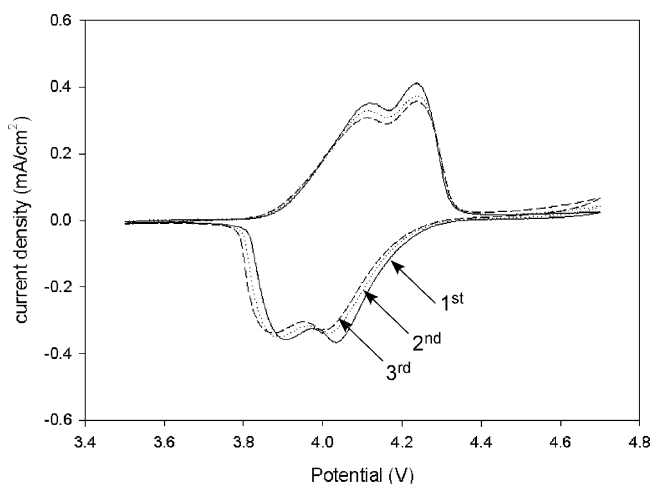


Fig. 2. TSC (thermal safety calorimetry) thermograms of (a: dotted line) 1.0 M  $\text{LiBF}_4/\text{EC} + \text{DEC}$  (2:1, v/v) gel, and (b: solid line) 1.0 M  $\text{LiBF}_4/\text{EC} + \text{DEC} + \text{TEP}$  (55:25:20) gel.

(55:25:20) in the temperature range of  $25\text{--}60^\circ\text{C}$ . For comparison, variation in the conductivity of the solution electrolyte, 1.0 M  $\text{LiBF}_4/\text{EC} + \text{DEC} + \text{TEP}$ , is also included. The polymeric gel electrolyte containing TEP exhibits a high value of the ionic conductivity,  $1.76\text{ mS cm}^{-1}$  at room temperature, along with a dimensionally stable self-standing form. The conductivity of the gel electrolyte increases with an increase in temperature, and apparently follows Arrhenius-type behavior. The ionic conductivity of the gel electrolyte containing TEP as a co-solvent was comparable to that with TMP [22]. Difference in the ionic conductivity between the gel electrolyte and the solution electrolyte was very small. Thus, non-flammable gel electrolyte with a high value of ionic conductivity and good dimensional stability can be used as an electrolyte for LIB.

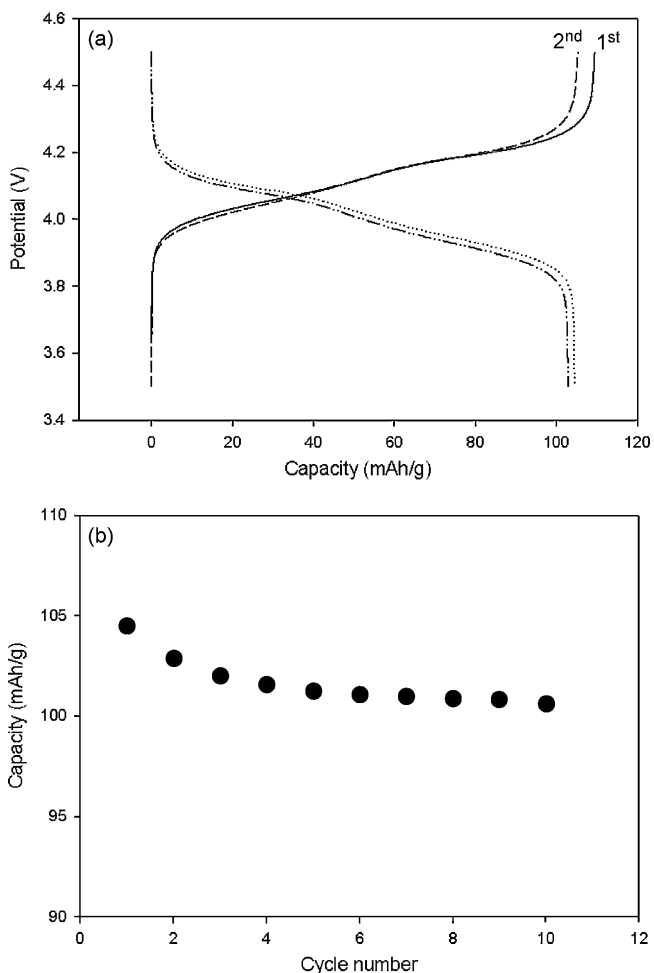
Thermal safety analysis of the polymeric gel electrolyte with and without fire-retardant solvent TEP was conducted, and the results are shown in Fig. 2. A broad endothermic peak observed at  $50^\circ\text{C}$  is due to the evaporation of the low boiling point solvent (DEC) which was left after the formation of gel electrolyte. The heat flow in the gel electrolyte increased suddenly at  $245^\circ\text{C}$ , which may be due to the decomposition of the electrolyte. The addition of TEP suppressed the abrupt heat flow in the electrolyte, and also reduced the amount of total heat generated from  $0.39\text{ W g}^{-1}$  to  $0.11\text{ W g}^{-1}$ . This 70% decrease in the heat flow observed with the addition of TEP in gel electrolyte indicates the active role of fire-retardant solvent in the electrolyte. However, we cannot estimate the exact nonflammability of the gel electrolyte using this experiment, but could ascertain it by a simple combustion test using burner flame [22].

Electrochemical behavior of the gel electrolyte with optimized composition, 1 M  $\text{LiBF}_4/\text{EC} + \text{DEC} + \text{TEP}$  (55:25:20) + PVdF-HFP (the mass ratio of the solution electrolyte and the polymer matrix was about 5:1), has been examined with the aim to use it as an electrolyte in LIBs. Fig. 3 represents cyclic voltammogram obtained for  $\text{LiMn}_2\text{O}_4$  electrode in the gel electrolyte at room temperature in 3.5–4.7 V potential range at a scan rate of  $0.1\text{ mV s}^{-1}$ . The voltammogram shows a pair of anodic peaks at around 4.1 V and 4.2 V, corresponding to the desorption of  $\text{Li}^+$ , whereas two cathodic peaks observed at 3.9 V and 4.0 V that relate to the insertion of  $\text{Li}^+$  in the oxide. These redox peaks point out that the desorption/insertion of  $\text{Li}^+$  from/into the spinal-type  $\text{LiMn}_2\text{O}_4$  are reversible in the gel electrolyte. In Fig. 4a is depicted the charge/discharge curves of the

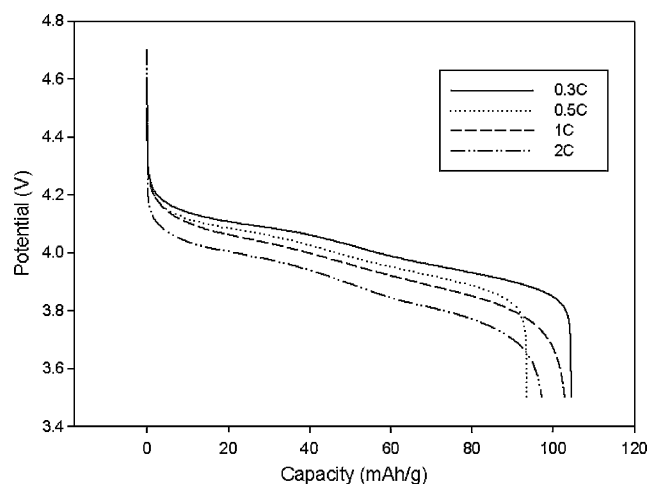


**Fig. 3.** Cyclic voltammogram for  $\text{LiMn}_2\text{O}_4$  electrode using gel electrolytes containing 1.0 M  $\text{LiBF}_4/\text{EC} + \text{DEC} + \text{TEP}$  (55:25:20). Working electrode:  $\text{LiMn}_2\text{O}_4$ , reference and counter electrodes: Li foil, scan rate:  $0.1 \text{ mVs}^{-1}$ .

$\text{LiMn}_2\text{O}_4$  electrode measured at 0.3C rate. The discharge capacity obtained for the first cycle was  $104.5 \text{ mAh g}^{-1}$ , which is almost the ideal capacity of the present material. Two different slopes were also observed in the charge–discharge curves, which are associated



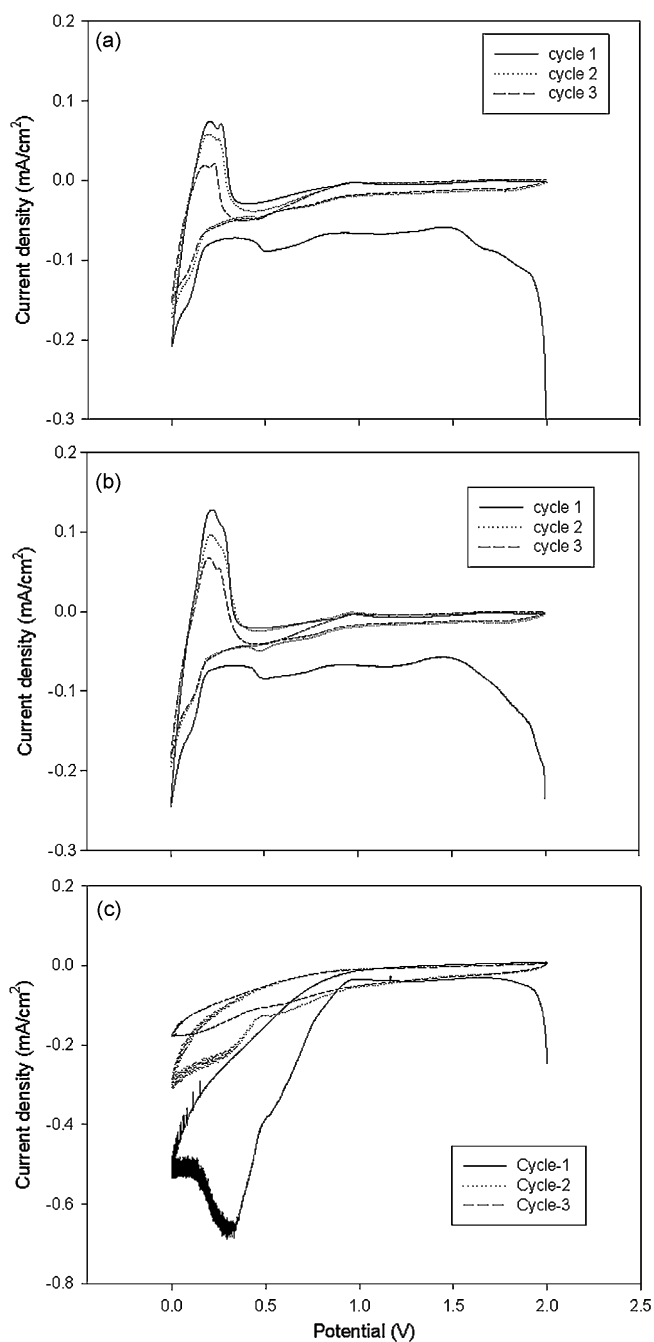
**Fig. 4.** (a) Charge/discharge curves of  $\text{LiMn}_2\text{O}_4$  electrode in 1.0 M  $\text{LiBF}_4/\text{EC} + \text{DEC} + \text{TEP}$  (55:25:20) gel electrolyte, and (b) variation of discharge capacity with cycle for  $\text{LiMn}_2\text{O}_4$  electrode in 1.0 M  $\text{LiBF}_4/\text{EC} + \text{DEC} + \text{TEP}$  (55:25:20) gel electrolyte.



**Fig. 5.** Discharge capacities of  $\text{LiMn}_2\text{O}_4$  electrode in 1.0 M  $\text{LiBF}_4/\text{EC} + \text{DEC} + \text{TEP}$  (55:25:20) gel electrolyte at different discharge rates.

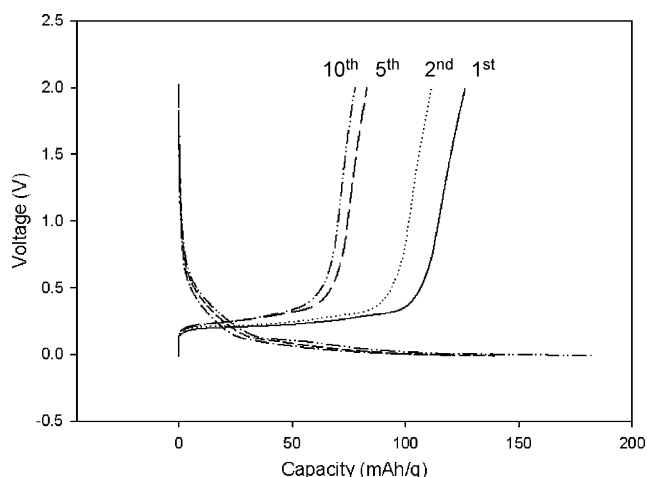
with the insertion/desertion of  $\text{Li}^+$  ion in two different available sites in  $\text{LiMn}_2\text{O}_4$ , as observed in the cyclic voltammogram. The reversibility of the electrochemical process is also observed in the charge/discharge curves. Fig. 4b indicates the change of discharge capacity with the cycles. After ten cycles, a loss of 3.72% capacity has been observed with respect to the first cycle. This shows good charge/discharge performance of the gel electrolyte for the cathode material. Fig. 5 shows the discharge curves for  $\text{LiMn}_2\text{O}_4/\text{gel}$  electrolyte half cell at different cycling rates. Usually the effective capacity of the cell is reduced when the cell is cycled at higher rates. We have found that the positive electrode with the gel electrolyte has sufficiently high capacity of  $102.7 \text{ mAh g}^{-1}$  even at high rate (2C) as compared to the capacity of  $104.5 \text{ mAh g}^{-1}$  at lower discharge rate (0.3C). This study reveals that the present gel electrolyte can be used in LIBs for high power applications.

Cyclic voltammetry was also conducted for a graphite/gel electrolyte half cell using Li as counter and reference electrodes in 0–2 V range at a scan rate of  $0.1 \text{ mVs}^{-1}$ , the result of which is shown in Fig. 6a. The voltammogram shows redox peaks observed in 0–0.3 V potential range vs.  $\text{Li}/\text{Li}^+$ . These peaks elucidate the insertion/desertion of lithium on the carbon material (graphite). Small irreversible current is also observed in 0.3–1.0 V potential range which may be due to the cathodic decomposition of the gel electrolyte on the graphite, which would help to form a solid electrolyte interface (SEI) film on the electrode. The cyclic voltammogram of the gel electrolyte without TEP, 1M  $\text{LiBF}_4/\text{EC} + \text{DEC}$  (2:1)+PVdF-HFP, is given in Fig. 6b. A comparison of Fig. 6a and b shows that there is no reduction of TEP in this potential range, which proves that TEP is electrochemically stable in the gel electrolyte. Also, cyclic voltammogram of the gel electrolyte containing TMP (trimethylphosphate), 1 M  $\text{LiBF}_4/\text{EC} + \text{DEC} + \text{TMP}$  (55:25:20)+PVdF-HFP, is also included in Fig. 6. There is no peak observed for insertion/desertion of  $\text{Li}^+$  for the negative electrode (Fig. 6c), which may be due to failure of formation of effective SEI film on the electrode material in the system containing TMP [8]. Cyclic voltammetry study proves that TEP is a better fire-retardant co-solvent for the development of nonflammable polymeric gel electrolyte. Charge/discharge characteristics of the gel electrolyte with graphite as working electrode and Li foil as both counter and reference electrode are shown in Fig. 7. Discharge capacity of  $126 \text{ mAh g}^{-1}$  has been obtained for the first discharge, which is lower than the ideal value of  $348 \text{ mAh g}^{-1}$  for this material. The low value of discharge capacity may be due to absorption of  $\text{BF}_4^-$



**Fig. 6.** Cyclic voltammograms of graphite electrode in (a) 1.0 M LiBF<sub>4</sub>/EC + DEC + TEP (55:25:20) gel, (b) 1.0 M LiBF<sub>4</sub>/EC + DEC (2:1) gel, and (c) 1.0 M LiBF<sub>4</sub>/EC + DEC + TMP (55:25:20) gel electrolytes. Working electrode: graphite (KS6), reference and counter electrodes: Li foil, scan rate: 0.1 mVs<sup>-1</sup>.

anion [23] on the graphite electrode, or due to the formation of a passivation layer on the graphite, which would be associated with decomposition of the electrolytic salt on the graphite electrode. Despite of the low capacity, nonflammable gel electrolyte with TEP shows better compatibility with the graphite electrode without any film forming additives, and also good self-standing gel with improved mechanical properties. In further studies, we will investigate other possibilities that can improve the compatibility of the gel electrolyte with the anode (negative electrode) material.



**Fig. 7.** Charge/discharge curves for graphite electrode in 1.0 M LiBF<sub>4</sub>/EC + DEC + TEP (55:25:20) gel.

#### 4. Conclusion

Gel electrolyte having composition of 1 M LiBF<sub>4</sub>/EC + DEC + TEP (55:25:20) and PVdF-HFP as a host polymer showed a high value of ionic conductivity of 1.76 mS cm<sup>-1</sup> at room temperature, which was comparable to that of the liquid electrolytes of 3.48 mS cm<sup>-1</sup>. Electrochemical tests on the nonflammable polymeric gel electrolyte based on 1 M LiBF<sub>4</sub>/EC + DEC + TEP (55:25:20) indicated the better performance of electrolyte for both cathode (LiMn<sub>2</sub>O<sub>4</sub>) and anode (graphite) materials as compared to other gel electrolytes containing TMP as fire-retardant solvent. There is no need to add SEI film-forming additives in the gel electrolytes which deteriorates its mechanical and thermal properties. Reversible discharge capacities of 104.5 mAh g<sup>-1</sup> and 126 mAh g<sup>-1</sup> were obtained for the positive and the negative electrodes, respectively. Good rate capability of the gel electrolyte with the positive electrode has been observed.

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