Using Vinylene Carbonate as Electrolyte Additive in Li-ion Batteries

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Abstract

Electrolytes having 1 m $LiBF_4$ salt concentration in the ratio of 1:1 (w/w) Ethylene Carbonate (EC): Dimethyl Carbonate (DMC) solvents were prepared. Vinylene Carbonate (1 %), as electrolyte additive, was added to prepared electrolyte solution. Free-standing SnO_2/Reduced Graphene Oxide (RGO) nanocomposite anode materials were fabricated by using SnO_2 nanopowders synthesized by sol-gel method and graphene oxide synthesized via Hummers' method. Obtained electrolytes and anode materials were used to assemble CR2016 Li-ion button cells. After electrochemical tests with 100 charge-discharge cycles, in order to investigate the effect of VC additive on the stability of anode material, the cells were disassembled. The anode materials were taken out and SEM method was applied to SnO_2/RGO nanocomposite anode material. The results indicated that VC forms beneficial SEI layer on the electrode material and provides capacity retention in Li-ion batteries.

Key words: Li-ion battery anodes, SnO_2/RGO nanocomposites, electrolyte additive, vinylene carbonate, electrochemical characterization.

1. Introduction

Lithium-ion batteries are considered as one of the most promising energy storage devices because of high energy density, high power density, long life and environmental friendliness [1]. Such benefits make Li-ion batteries as attractive candidates for portable electronics such as laptops, cameras, and mobile phones. They are currently utilized to drive hybrid electric vehicles (HEV) and expected to power electric vehicles (EV) in the near future [2].

As anode materials, tin oxide based materials have attracted much attention for replacing the current carbon-based materials for Li-ion batteries because of their high theoretical discharge capacity (1491 mAhg^{-1}) [3]. However, during the Li insertion/extraction process, a huge volume expansion of metal oxides takes place inducing cracking and pulverization of the anodes.

To tackle this problem, metal oxide/graphene composites are proposed promising anodes due to the superlative mechanical strength and resilience of graphene sheets [4]. Graphene which is a two-dimensional aromatic monolayer of carbon atoms has attracted a great deal of interest as a promising anode material in battery applications, because of its superior electrical conductivity, high specific surface area, and structural flexibility [5].

Generally, Li-ion battery electrolytes comprise of cyclic alkyl carbonates, such as ethylene carbonate (EC), and linear alkyl carbonates, such as dimethyl carbonate (DMC) and lithium-bearing salts [6]. Having a smaller anionic size relative to commercial electrolyte salt $LiPF_6$,

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$LiBF_4$ has been widely studied as an electrolyte salt. Decreasing the anionic size increases the ionic conductivity, due to the higher mobility of the BF_4^- ions according to PF_6^- ions [7]. Several reactive additives, such as vinylene carbonate (VC) to electrolyte solutions improve the performance of the anodes in Li-ion batteries. VC which is both a highly strained cyclic alkyl carbonate and has a polymerizable double bond is indeed a highly interesting additive for Li-ion batteries. [8]. Due to these features, VC as an additive to the electrolyte has been proposed to improve the performance of the Li-ion batteries [9].

In this work, tin dioxide (SnO_2) powder was prepared by a sol-gel technique and its nanocomposite with reduced graphene oxide (RGO) was produced by vacuum filtration giving a high capacity anode material for Li-ion batteries. For electrolyte solution, 1 m $LiBF_4$ salt was dissolved in EC:DMC solvents (1:1, w/w). In order to determine the effect of electrolyte additive on SnO_2/RGO nanocomposite anode's cycling efficiency, the appropriate amount of VC (1 %) was added to $LiBF_4$ electrolyte. CR2016 cells were assembled in a glove box (MBraun-Labstar). The cells were charged and discharged at 25 °C between fixed voltage limits (2.5 V to 0.01 V) at a constant current density on a BST8-MA MTI model battery tester with 0.2 C charge-discharge rate. Cyclic voltammetry (CV) was performed at the scan rate of 0.1 mVs^{-1} and electrochemical impedance spectroscopy (EIS) measurements were carried out using Gamry Instrument applying a sine wave of 10 mV amplitude over a frequency range of 1000 kHz-0.01 Hz. After electrochemical tests, the cells were disassembled and the anode materials were characterized by scanning electron microscopy (SEM).

2. Materials and Method

2.1. Preparation of SnO₂/RGO buckypaper nanocomposites

For the production of SnO_2 powder, sol-gel method was applied. The SnO_2 precursor sol was prepared from 8 mmole $SnCl_2.2H_2O$ (tin (II) chloridedihydrate) and its chloride ions were removed from tin solution with the addition of a stoichiometric ratio of NH_3 (25%) solution. After the precipitation of tin hydroxide ($Sn(OH)_n$, n:2 or 4), the solid was filtered and washed with diluted NH_3 solution. The final precipitate was dissolved in glacial acetic acid (CH_3COOH), and then 20 mL ethylene glycol (HOC_2H_4OH) was added to each solution in order to form complex with tin cations. The stirring was continued from 50 °C to 80 °C until the acetic acid to be removed from the obtained sol and at the end of stirring; gels were obtained and dried in an oven at 150 °C in air. Finally, precalcination step was performed on dried gels at 300 °C, and samples were calcined at 500 °C in air at a heating rate of 2 °C/min and held at the same temperature for 2h [3].

In order to synthesize SnO_2/RGO buckypaper nanocomposites, firstly graphite oxide was synthesized from pre-treated graphite powders via modified Hummers' method [10]. To produce graphene oxide and its nanocomposite with SnO_2, graphite oxide was exfoliated by ultrasonication together SnO_2 nanopowders. For this, 45 mg of as-synthesized graphite oxide and 45 mg SnO_2 was dispersed in 50 mL of distilled water and sonicated for 1 h to increase the interlayer distances between graphite oxide layers to obtain graphene oxide. Then, the solution

was filtered on PVDF membrane (Millipore, Durapore Membrane) by vacuum filtration technique. Then, after vacuum filtration, the SnO_2/GO paper was peeled off from the PVDF membrane, reduced in distilled hydrazine solution. SnO_2/RGO free-standing paper was obtained and used as anode in CR2016 Li-ion cell.

2.2. Fabrication of Electrolyte Solutions

To prepare electrolytes, $LiBF_4$ (Sigma-Aldrich, 99.998%) was used as salt; Ethylene Carbonate (EC) (Merck, ≥ 99%) and Dimethyl Carbonate (DMC) (Merck, ≥ 99%) mixture was used as solvent. The optimum ratio of EC:DMC was selected as 1:1 (w/w) since it provides higher discharge capacity. Hence, this solvent ratio was kept constant in preparing electrolytes. On the other hand, $LiBF_4$ salt concentration was selected as 1 m (molality, moles $LiBF_4$ per kilogram of solvent) in the electrolytes. For this purpose, firstly EC solid was weighed in the ratio of 1:1 (w/w, EC:DMC) and DMC liquid was added. Following these steps, the mixture was stirred until EC dissolves in DMC. After that, calculated amounts of $LiBF_4$ salt was added to the prepared solvents and mixed for 10 hours to get homogeneous solutions. In order to determine the effect of electrolyte additive on SnO_2/RGO nanocomposite anode's cycling efficiency, two parallel electrolyte solutions were prepared (without and with Vinylene Carbonate, VC). The appropriate amount of VC (1 %) was added to first electrolyte solution and the second sample did not include VC. After adding VC additive, the electrolyte solution was stirred for 4 hours to get homogeneous solutions.   All the electrolyte preparations were carried out in a glove box in order to protect the solutions from moisture and prevent oxidation of the electrolytes. Additionally, the prepared electrolytes were stored in amber bottles to prevent any degradation effect arising from sun light.

2.3. Electrochemical cell preparation and measurements

As working electrode SnO_2/RGO buckypaper nanocomposite anodes were used. Metallic lithium and polypropylene (PP) were used as cathode and separator, respectively. The prepared $LiBF_4$ electrolyte solutions, with VC and without VC, were used as electrolyte. CR2016 cells were assembled in a glove box (MBraun-Labstar). The cells were charged and discharged at 25 °C between fixed voltage limits (2.5 V to 0.01 V) at a constant current density on a BST8-MA MTI model battery tester. The charge discharge rate was chosen as 0.2C for discharge capacity measurements. Cyclic voltammetry (CV) was performed at the scan rate of 0.1 mVs^{-1}.

2.4. Disassembling the cells

In order to investigate the nanocomposite anode materials' stability after 100 charge-discharge cycles, the cells were disassembled and the anode materials were taken out, rinsed with DMC and dried at 35°C for four hours. Obtained anode materials were analyzed by scanning electron microscopy SEM (SEM-JEOL-JSM 6060LV) to examine the effect of electrolyte solutions on the stability of nanocomposite anode materials.

3. Results and Discussion

In order to investigate the effect of Vinylene Carbonate (VC) as additive in electrolyte solution on the electrochemical performance of nanocomposite SnO_2/RGO anode material, electrochemical tests were performed at room temperature. The comparison of discharge capacities of the SnO_2/RGO nanocomposite anodes depending on VC additive is given in Figure 1. For the cell including electrolyte with VC additive, the capacity retention is higher than the cell including electrolyte without VC additive after 100 charge-discharge cycles. Table 1 shows 1st, 20th, 50th and final (for 100 cycles) discharge capacities of the cells including without VC and with VC additive. As can be seen from Table 1, the specific capacities obtained in the first cycles are 1485.2 and 1408.2 mAh g^{-1}, in the 20th cycle 221.6 and 548.6 mAh g^{-1} for the cells including 1 m $LiBF_4$ electrolyte without VC and with VC additive, respectively. And in the 50th cycle, the capacities of the SnO_2/RGO anode materials are around 101.1, 304.1 mAh g^{-1} and in the final (100th) cycle 33.3, 179.8 mAh g^{-1} for the cells including electrolyte without VC and with VC additive, respectively. It was found that the cell including 1 m $LiBF_4$ electrolyte without VC additive indicated a little higher initial capacity compared with the cell prepared with VC additive. However, for the cell including electrolyte without VC showed dramatically capacity fading. When VC additive was added in the electrolyte solution, the cell presented higher capacity retention. The difference on cycle life and capacity of SnO_2/RGO nanocomposite anodes in the cells including $LiBF_4$ electrolyte with VC and without VC electrolytes may be referred to the different properties of SEI layer which formed in initial cycles on the anode surface [11].
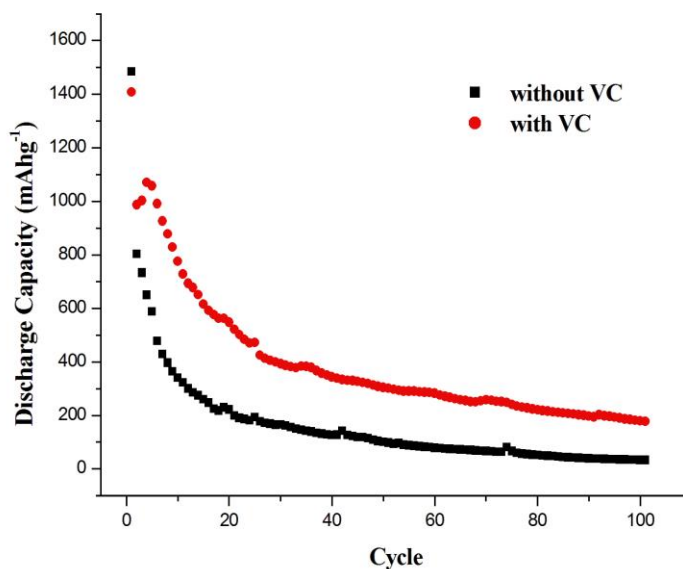

Figure 1. Electrochemical discharge capacity of the anodes for the cells including electrolyte with VC and without VC additive

Table 1. The comparison of discharge capacities of nanocomposite anodes for the cells including electrolyte with VC and without VC additive

Samples	1st cycle	20th cycle	50th cycle	100th cycle
Without VC	1485.2 mAh g^{-1}	221.6 mAh g^{-1}	101.1 mAh g^{-1}	33.3 mAh g^{-1}
With VC	1408.2 mAh g^{-1}	548.6 mAh g^{-1}	304.1 mAh g^{-1}	179.8 mAh g^{-1}

In order to investigate the electrochemical properties of the SnO$_2$/RGO nanocomposite electrodes in the cell with VC additive during the charge–discharge process, cyclic voltammetry (CV) measurements were applied. Figure 2 shows CV curves of the cell including VC additive in electrolyte solution. The alloying and de-alloying (intercalation) processes of lithium with SnO$_2$ and graphene were carried out over the potential range of 2.5–0.01 V vs. Li/Li$^+$ at a scanning rate of 0.1 mV s^{-1}.
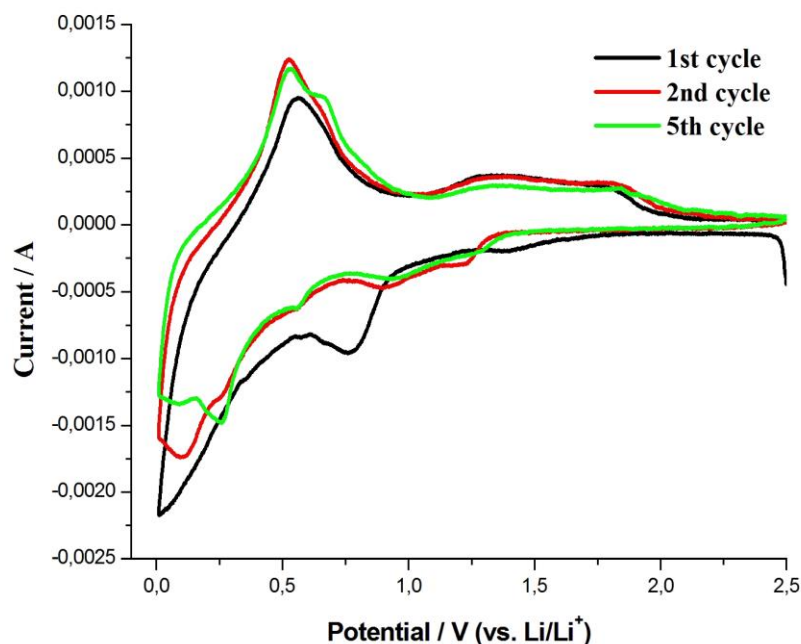
Figure 2. Cyclic voltammogram curves of SnO$_2$/RGO anode including electrolyte with VC additive between potential range of 2.5–0.01 V for five cycles, the scan rate is 0.1 mV s^{-1}

The electrochemical reaction mechanism for the SnO$_2$/Li cell is described as follows [12]:

$$SnO_2 + 4Li^+ + 4e^- \longrightarrow Sn + 2Li_2O \tag{1}$$
$$Sn + xLi^+ + xe^- \rightleftharpoons Li_xSn \ (0 \leq x \leq 4,4) \tag{2}$$
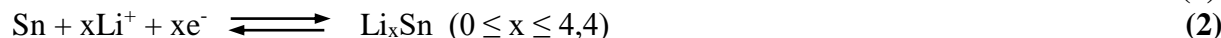
For the SnO_2/RGO anode sample, the CV curves were recorded for 5 cycles. An irreversible first reaction (1) is observed during the first discharge. The Li-inserted SnO_2 forms amorphous Li_2O and metallic Sn with a reduction peak (>1V) [13]. Electrochemically inactive Li_2O phase formed during the first insertion reduces the capacity of anode. At about 0.75 V, the sharp and broad negative-going peak can only be observed during the first cathodic sweep, which derives from decomposition of the electrolyte and the formation of an SEI film on the anode surface [14]. The reversible reaction (2) of the metallic Sn with lithium subsequently leads to the formation of Li-Sn alloys with the composition of $Li_{4.4}Sn$ [15] and appears as the reduction peak below 0.5 V. At about 0.5 V, the oxidation peaks can be assigned to the dealloying of Li_xSn [16]. Additionally, at 1.23 V a broad oxidation peak which may relate to the decomposition of Li_2O is found [12]. Reduction peak observed at 0.02 V and oxidation peak at 0.2 V in CV curves can be referred to lithium-ions insertion into and extraction from the graphene layers.
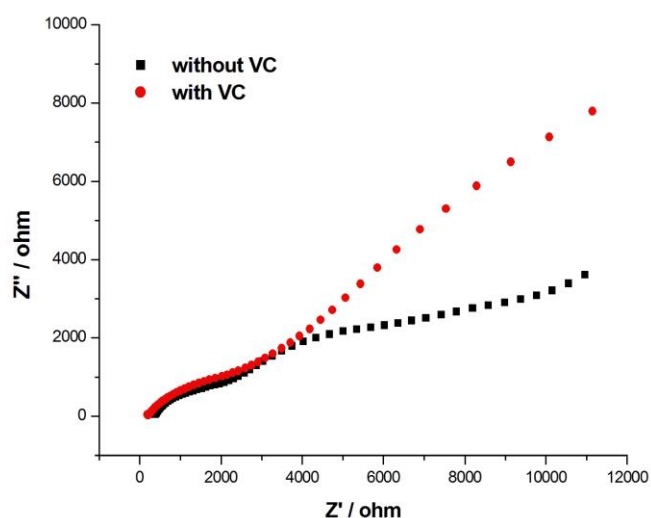

Figure 3. Impedance curves belong to the cells including 1m $LiBF_4$ electrolyte with VC and without VC additive

In order to analyze impedance of the cell electrochemical impedance spectroscopy (EIS) measurements were carried out at room temperature. In order to achieve stable SEI formation and the percolation of electrolyte through the electrode materials, the impedance measurement was performed after running charge–discharge for 5 cycles. According to the previous literature, the Nyquist plot of a battery can roughly be divided into three parts. The high-frequency semicircle can be referred to the contact resistance (R_s) occurring due to the SEI film; the medium-frequency semicircle is related to the charge-transfer resistance (R_{ct}) at the interface between the electrolyte and the electrode material, and the inclined lines correspond to the Li diffusion process inside the electrode material [17]. And the contact resistance between the electrode and current collector is known as R_c [18].

Resistance of electrolyte solution (R_s) of the cell is analyzed by the solution which is between the counter electrode and working electrode surface. In addition, dissolved ion concentration in

electrolyte solution and conductance of the solution affects the cell electrolyte solution resistance (R_s) [19]. Impedance curves belong to the cells including 1m $LiBF_4$ electrolyte with VC and without VC are shown in Figure 3. The distance between zero point and initial point of Nyquist curve on the X-axis indicates R_s value of the cell. It can be seen that R_s value of the cell including electrolyte with VC is lower than the other cell.
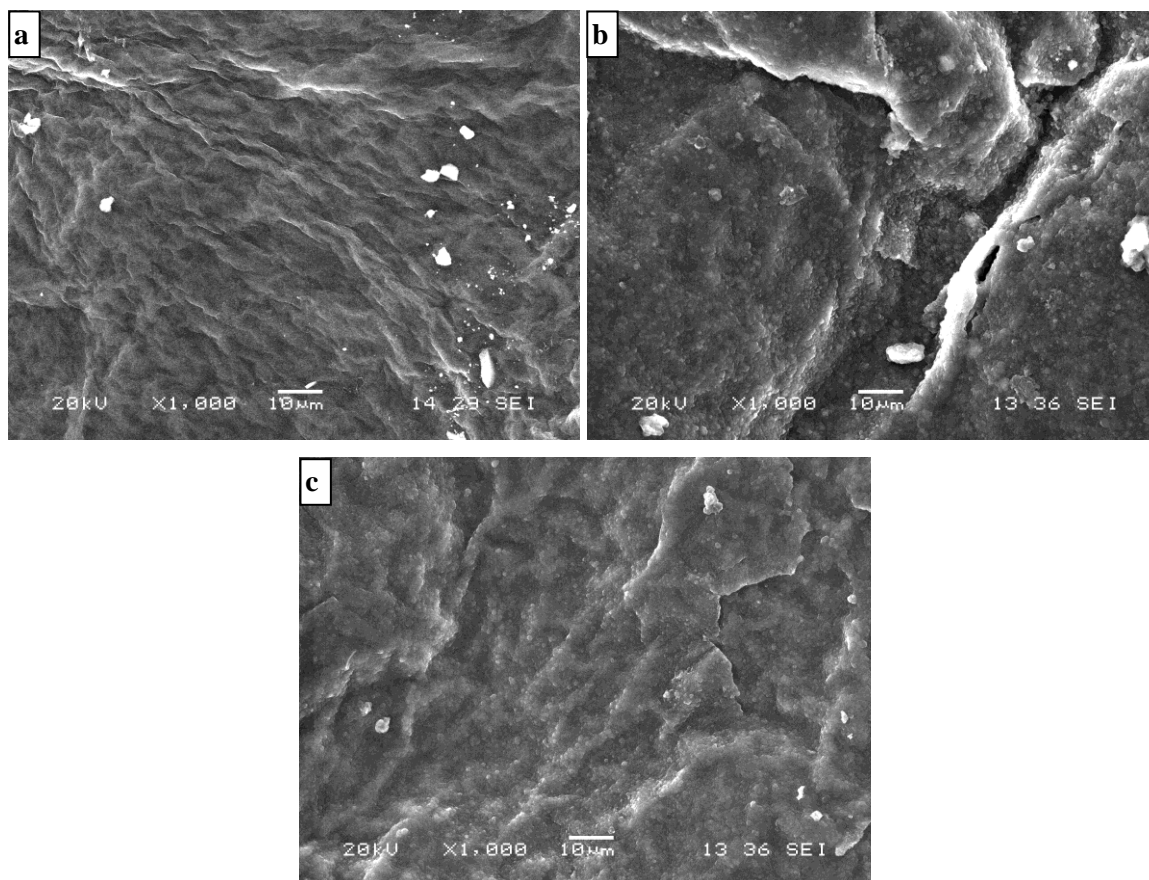

Figure 4. SEM images of the surface of a) pristine anode, b) anode removed from the cell including electrolyte without VC and c) with VC additive

Figure 4-a shows SEM image of SnO_2/RGO nanocomposite anode structure before electrochemical test. Figure 4-b and c indicate SEM images of the anodes removed from the cell including electrolyte without VC and with VC additive, respectively. As can be seen from the images, for the anode material which cycled with the electrolyte added VC, the morphology of the composites before and after electrochemical test seems similar structure. However, the surface of the anode which taken out from the cell including electrolyte without VC additive shows inhomogeneous surface with some cracks and agglomeration after 100 cycle when we compare with the anode removed from the cell including VC additive. Because, the electrolyte solution including VC additive leads to forming beneficial SEI layer on the anode surface and protects the anode from pulverization and mechanical disintegration.

Conclusions

Free-standing SnO_2/RGO nanocomposite anodes were produced to obtain high-capacity anode material. In EC:DMC solvents (EC:DMC / 1:1) 1 m $LiBF_4$ electrolyte solutions prepared with VC and without VC additive. The effect of VC additive in electrolyte solution on SnO_2/RGO nanocomposite anode was investigated via electrochemical analysis. The results showed that discharge capacities were 33.3 and 179.8 $mAhg^{-1}$ after 100 charge-discharge cycles for the cells including electrolyte without VC and with VC additive, respectively. For the cell including electrolyte without VC additive, higher initial irreversible discharge capacity exhibited compared with the cell including electrolyte with VC additive. However, after initial cycles discharge capacity of the cell including electrolyte without VC additive dramatically decreased. Discharge capacity of the cell including VC electrolyte additive shows high stability. Also electrochemical test results are compatible with SEM results. The image of the anode material which taken out from the cell including VC additive is almost the same with pristine anode material. On the contrary, SEM image of the anode removed from the cell including electrolyte without VC additive showed inhomogeneous surface after 100 charge-discharge cycles. Consequently, when Vinylene Carbonate is used in electrolyte solution as additive, it forms polymeric SEI layer on electrode surface and protects anode surface during charge discharge cycles. Hence, VC provides capacity retention due to these features.

Acknowledgements

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