



Alternative Multifunctional Cyclic Organosilicon as an Efficient Electrolyte Additive for High Performance Lithium-Ion Batteries



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ARTICLE INFO

Article history:

Received 13 May 2017

Received in revised form 18 September 2017

Accepted 18 September 2017

Available online 20 September 2017

Keywords:

Lithium-ion battery

Organosilicon compounds

Electrolyte additive

High potential

Cathode electrolyte interface

ABSTRACT

Three kinds of functional organosilicon electrolyte additives, i. e. octamethylcyclotetrasiloxane (D4), octamethylcyclotetrasiloxane (OMCTS) and 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (ViD4), are firstly used to produce high-performance $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode for rechargeable Lithium-ion batteries (NCM622/Li half-cell) at a high potential. The electrochemical performance tests at 4.5 V suggest that ViD4 is the most promising electrolyte additive than its counterparts. Moreover, the prepared NCM622/Li half-cell with 0.5 wt.% ViD4 exhibits an improved energy density of 187.2 mAh g^{-1} and a good discharge capacity retention of 83.6% at 1C rate after 150 cycles at 4.5 V, which is relatively higher than that with D4 (81.3%), OMCTS (81.9%) and much better than the bare electrolyte (76.1%). The electrochemical characterizations, density functional theory calculation and surface analysis provide strong evidences that combined effects of the Si-O bond and vinyl functional group in ViD4 can promote the formation of a uniform cathode electrolyte interphase (CEI) film. Moreover, the ViD4-incorporated CEI film effectively enhances the interfacial stability between the NCM622 cathode and the electrolyte by suppressing the continuous decomposition of carbonate-based electrolyte and the exfoliation of these decomposition products. Hence, the ViD4-containing electrolyte shows a promising potential for the application in high energy density lithium-ion batteries.

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1. Introduction

Rechargeable Li-ion batteries (LIBs) have been widely used in numerous commercial applications, from digital technologies to electric vehicles [1–3]. It is of a great interest for battery engineers and manufacturers to fabricate the advanced LIBs with high energy density. By utilizing the Li-rich or Ni-rich layered transition metal oxides $[\text{Li}_{1+x}(\text{Ni}_y\text{Co}_z\text{Mn}_{1-y-z})\text{O}_2]$, NCM] and elevating the working potential, the energy density of LIBs can be extensively enhanced [4,5]. However, the NCM cathode usually suffers from an inferior stability and a low capacity retention at a high cut-off potential. The reasons can be ascribed to the unstable surface layer gradual exfoliation, the continuous electrolyte decomposition and the transition metal ion dissolution [6–8]. Therefore, it is extremely necessary to stabilize the surface structure of NCM cathode at a high potential to develop an advanced LIBs with high energy density NCM.

To solve these problems, numerous strategies have been explored, such as coating, doping and exploring different electrolyte additives [9,10]. Comparing with coating and doping strategies, exploring different electrolyte additives is a much more facile and economical strategy. This electrolyte additive is believed to oxidize preferentially to the solvent molecule in the bare electrolyte, resulting in a protective cathode electrolyte interphase (CEI) film formed on the surface of NCM. This protective CEI film will suppress the electrolyte decomposition and protect the NCM from crystal destruction [11]. Thus, different kinds of electrolyte additives matching for different electrolyte systems have been reported, such as phosphorus-based, boron-based, silicon-based and sulfones electrolyte additives [12]. Among them, silicon-based electrolyte additives have been attracted growing attentions due to their low viscosity, low flammability, non-volatile and nontoxic [13–15]. More importantly, silicon-based electrolyte additives are facile to modify with functional groups to modulate the surface chemistry of cathode. For example, Huang et al. hold that 1,4-bis(trimethylsilyl)-2,5-dimethoxybenzene (BTMSDB) can provide superb overcharge protection of LiFePO_4 electrode [1]. Similarly, Amine et al. find that the silane compounds with Si-O bands

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exhibit excellent high voltage stability, which makes them have great potential for applying in Li-ion batteries with high potential cathode materials [16]. Zhang et al. believe that Si-O bond functionalized octamethylcyclotetrasiloxane (D4) can effectively remove corrosive substances in the electrolyte system [17]. Moreover, Vinyl group modified vinyl-Tris-(methoxydiethoxy) silane (VTMS) is found to be efficient in decreasing the flammability of the electrolytes, enhancing thermal stability and improving the safety [18,19]. Furthermore, the Si-N bond functionalized organosilicon has also been proposed to scavenge moisture and Lewis acids in the electrolyte [20,21]. Inspired by these exciting reports, we believed that functionalized silicon-based electrolyte additives could be efficient additives for improving the cycling stability and energy density of LIBs. However, limited literature pays attention to the beneficial effects of the silicon-based electrolyte additives on Ni-rich NCM, such as $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622), especially at a high potential.

In this paper, organosilicon electrolyte additives with the same cyclical structure but different functional groups, such as D4 with Si-O bond, octamethylcyclotetrasilazane (OMCTS) with Si-N functional bond as a substitute for Si-O bond of D4, and 2,4,6,8-Tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (ViD4) with vinyl functional group as a substitute for methyl group of D4, are systematically studied as electrolyte additives to improve cycling stability and energy density of NCM622/Li half-cell at a high potential. The effect of different D4 concentrations on the cycling stabilities of NCM622/Li half-cells are systematically evaluated by a surface 3D plot via galvanostatic charge-discharge tests at 4.3 V. Furthermore, the cycling stabilities and initial coulombic efficiencies of NCM622/Li half-cells with D4 (0.5 wt%), OMCTS (0.5 wt%) and ViD4 (0.5 wt%) are investigated at a high potential (4.5 V). Density functional theory calculation in conjunction with electrochemical experiments and electrode analyses imply that the cycling stability and interfacial stability of the fabricated NCM622/Li half-cell at 4.5 V can be simultaneously improved by adding proper content of ViD4 into the bare electrolyte. Therefore, the proposed NCM622/Li half-cell with electrolyte additives of ViD4 organosilicon is a promising candidate for constructing Lithium-ion batteries with good cycling stability and high energy density at a high potential.

2. Experiments

2.1. Synthesis of NCM622

The precursor of NCM622 was purchased from Ningxia Orient Tantalum Industry CO. LTD. The $\text{LiOH}\cdot\text{H}_2\text{O}$ (purchased from Aladdin) was homogeneously mixed with the $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ in a molar ratio of 1.05:1 by ball-milling at a rotation speed of 250 r min^{-1} . After ball milling for 2 h, the mixture was calcined in a tubular furnace at 835°C in an air atmosphere for 12 h and subsequent with a natural cooling treatment.

2.2. Cathode and electrolyte preparation

The cathode electrode was prepared by mixing 80 wt% NCM622, 10 wt% Super P (Timcal) and 10 wt% polyvinylidene (PVDF). Notably, the PVDF was previously dissolved in N-methyl-pyrrolidone (NMP) to obtain a 3.5 wt% solution. Then the slurry was coated onto Al foil, and dried in vacuum at 90°C for 12 h. The dried Al foil was cut into pole disc with a diameter of 13 mm. The mass loading of each pole disc was about 2 mg cm^{-2} . The cathode and steel battery shell were dried in vacuum at 105°C before assembling. The CR2032 coin cells for electrochemical measurements were assembled in a glovebox (Dellix) filled with Ar gas. The half-cell was consisted of NCM622 cathode, Li metal foil anode and

microporous polypropylene membrane separator. The diameter of Li metal foil anode was 16 mm. Moreover, the same procedure was used for the cathode and anode symmetric cells with fresh bare electrolyte. Both of the reassembled symmetric cells were kept stand for 10 h before EIS testing and the open-circuit-voltage (OCV) of each symmetric cell was below 50 mV.

The bare electrolyte was purchased from Hairong CO. LTD. with 1 M LiPF_6 dissolved in ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) mixture solvent (1:1:1 in volume ratio). For the modified electrolyte, D4 was added as an additive of 0.2, 0.5, 1, 2, 3 or 5% by weight. OMCTS and ViD4 were also chosen as electrolyte additive for comparison and assembled in the same way. All the cyclic organosilicons were purchased from Macklin Company (Shanghai Macklin Biochemical Co., Ltd, China) and used without further purification.

2.3. Measurements

The galvanostatic charge-discharge test was performed on Neware CT-4008-5V5ma battery testing system in the potential range of 2.8–4.3 V and 3.0–4.5 V vs. Li/Li^+ . Before cycling tests and storage experiments, cells were activated by galvanostatic charge-discharge at 0.2C for 3 cycles, where 1C was set as 160 mA g^{-1} . Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried on PARSTAT 2273 Electrochemical System (Princeton). CV measurement was performed at a voltage range of 3.0–4.5 V with various scan rates (0.2, 0.4, 0.6 and 0.8 mV s^{-1}). EIS measurements were operated at the open potential in the frequency range of 20 mHz to 100 kHz at the full charge state for NCM622/Li half-cell and at OCV state for cathode and anode symmetric cells. Strip-plate tests were carried out in Li/Li symmetric coin cells during galvanostatic cycling [$+0.5\text{ mA cm}^{-2}$ (30 min) \rightarrow Rest (10 min) \rightarrow -0.5 mA cm^{-2} (30 min) \rightarrow Rest (10 min)].

The cells after 150 cycles at 4.5 V were disassembled in an argon filled glove box (Dellix). Both the cycled NCM622 cathode and lithium foils were rinsed in DMC for three times. The lithium foils were dissolved in dilute nitric acid in 25 ml volumetric flask for 5 days before ICP-MS analysis. The surface morphologies of fresh and cycled NCM622 were analyzed by scanning electron microscopy (SEM; INCA Pen-taFET $\times 3$). The chemical composition of the surface layer on NCM622 was confirmed by X-ray photoelectron spectroscopy (XPS, phi5600)

2.4. Computations

The energy levels of Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) of organic molecules were calculated by the GAMESS program package [20–22]. The molecular structures and energy of solvent molecules, vinylene carbonate (VC) and ViD4 were optimized by density functional theory (B3LYP) methods with 6-311G(d,p) basis sets.

3. Results and discussion

As mentioned above, Ni-rich NCM cathodes usually show high specific capacities but suffer from inferior stabilities. Their cycling stabilities can be effectively enhanced by adding the organosilicon electrolyte additives. Considering that the D4 is one of the most common silicon-based electrolyte additives, the effect of D4 on the performance of NCM622 is firstly evaluated in this work. As shown in Fig. 1a, the cycling performance of NCM622/Li half-cells with various D4 concentrations at 1C rate in the voltage range of 2.8–4.3 V are analyzed by a 3D surface plot. The idea of drawing the 3D surface plot is coming from the topographic map (Fig. S1) that

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