



Significantly improved cyclability of lithium manganese oxide under elevated temperature by an easily oxidized electrolyte additive



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HIGHLIGHTS

- Cyclability of LiMn₂O₄ under elevated temperature can be improved significantly by DMPP.
- DMPP can be easily oxidized on LiMn₂O₄ at the potential before lithium extraction.
- Cathode interphase is formed from DMPP without incorporation of electrolyte.
- Crystal destruction of LiMn₂O₄ is prevented and electrolyte decomposition is suppressed.

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ABSTRACT

Spinel lithium manganese oxide, LiMn₂O₄, is a promising cathode for lithium ion battery in large-scale applications, because it possesses many advantages compared with currently used layered lithium cobalt oxide (LiCoO₂) and olivine phosphate (LiFePO₄), including naturally abundant resource, environmental friendliness and high and long work potential plateau. Its poor cyclability under high temperature, however, limits its application. In this work, we report a significant cyclability improvement of LiMn₂O₄ under elevated temperature by using dimethyl phenylphosphite (DMPP) as an electrolyte additive. Charge/discharge tests demonstrate that the application of 0.5 wt.% DMPP yields a capacity retention improvement from 16% to 82% for LiMn₂O₄ after 200 cycles under 55 °C at 1 C (1C = 148 mAh g⁻¹) between 3 and 4.5 V. Electrochemical and physical characterizations indicate that DMPP is electrochemically oxidized at the potential lower than that for lithium extraction, forming a protective cathode interphase on LiMn₂O₄, which suppresses the electrolyte decomposition and prevents LiMn₂O₄ from crystal destruction.

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1. Introduction

Lithium ion battery has been widely used in electronic devices due to its longer cycle life and higher energy density than other secondary batteries [1,2]. However, we still face issues when we use it as power sources in large-scale application such as in electric vehicles [3–5]. Among these issues, it is the most challenging to reduce the price of lithium ion battery, which is far higher than gas engine in vehicles. Cobalt-containing compounds such as layered

lithium cobalt oxide (LiCoO₂) and olivine lithium iron phosphate (LiFePO₄) dominate cathodes of currently commercialized lithium ion battery, but they account mainly for the high price due to the rare resource of cobalt and the complicate synthesis of LiFePO₄ [6–11]. Additionally, lithium ion battery based on these cathodes work under low voltage, which cannot provide high energy density for large-scale application [12–16].

Spinel lithium manganese oxide, LiMn₂O₄, is a promising cathode for lithium ion battery in large-scale applications, because it possesses many advantages compared with LiCoO₂ and LiFePO₄, including naturally abundant resource, environmental friendliness, high specific capacity, and high and long work potential plateau [17–23]. Its poor cyclability, however, limits its application, especially under high temperature [24,25]. Under fully charged state of

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LiMn_2O_4 , the electrolyte might decompose through direct electrochemical oxidation or interaction with charged LiMn_2O_4 , forming HF [26,27], which causes the dissolution of Mn^{2+} from LiMn_2O_4 , leading to the poor cyclability of LiMn_2O_4 [28–30].

Much effort has been made to improve cyclability of LiMn_2O_4 , which is mainly focused on the improvement in structural stability by substituting transition metals (Co, Ni, Cr, etc.) for Mn or F for O partially and coating with inert materials [31,32]. Unfortunately, these approaches cannot avoid the electrolyte decomposition. Furthermore, the additional processes increase synthetic cost and the introduction of inert components reduces the specific capacity of LiMn_2O_4 . To reduce the electrolyte decomposition, some solvents such as lactone [33] and sulfone [34,35] was used to replace the conventional carbonate solvents, but this replacement yields low ionic conductivity of the electrolytes and poor interfacial compatibility of the electrolytes with cathode.

Recently, much attention has been paid to electrolyte additives for the cyclability improvement of high voltage cathodes such as 4.5 V layered oxides or 5.0 V spinel oxides [36,37]. It has been found that a protective cathode interphase can be formed by applying electrolyte additives, which can protect cathode from crystal destruction and suppress electrolyte decomposition under high voltage [38–42]. Accordingly, several electrolyte additives have been developed to improve cyclability of LiMn_2O_4 at high temperature [43–46]. Unfortunately, the improvement is not satisfying. For example, 3,3'-sulfonyldipropionitrile was reported in a new publication as an electrolyte additive for improving cyclability of LiMn_2O_4 , yielding a capacity retention of only 70.3% after 200 cycles at 1 C under 55 °C between 3 and 4.3 V [46].

The formation of a protective cathode interphase depends on the oxidation decomposition potential and molecule structure of the electrolyte additives. On the one hand, the additives should be oxidized preferentially to the electrolyte to build protective cathode interphases; on the other hand, the molecule structure of the additives contributes to the physical and chemical stability of the cathode interphases through the incorporation of their oxidation decomposition products. Comparatively, the preferential oxidation of the additives is more important for the formation of protective cathode interphases because the incorporation of electrolyte decomposition products into cathode interphases can be avoided if the cathode interphases is formed before electrolyte decomposition. Recently, we have found that dimethyl phenylphosphonite (DMPP) could be used as an electrolyte additive for cyclability improvement of 5.0 V spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [47]. Like most of electrolyte additives that have been reported in literature, DMPP does not exhibit a significantly preferential oxidation to electrolyte on the spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and the incorporation of electrolyte decomposition products into cathode interphases is inevitable. In this work, we report a new finding that DMPP can be oxidized easily on LiMn_2O_4 at the potential before lithium extraction, yielding an excellent cyclability of LiMn_2O_4 under high temperature.

2. Experimental section

2.1. Preparation

Dimethyl phenylphosphonite (DMPP) was purchased from Alfa Aesar Technology Co. Battery-grade carbonate solvents and lithium hexa-fluorophosphate (LiPF_6) were provided by Guangzhou Tinci Materials Technology Co. Ltd, China. A base electrolyte (1.0 M LiPF_6 in ethylene carbonate (EC)/ethyl methyl carbonate (EMC), EC/EMC = 3:7, in volume) and DMPP (0.5 and 1 wt.%) as additive were used. Electrolytes were prepared in an Ar-filled glove box (MBraun, Germany). The contents of water in the electrolytes were controlled below 20 ppm, which were determined by Karl-Fisher 831

Coulometer (Metrohm, Switzerland). LiMn_2O_4 electrode was prepared by coating a slurry of 80 wt.% LiMn_2O_4 (Hunan Reshine New Material Co., Ltd), 10 wt.% acetylene carbon black, 10 wt.% PVDF binder on Al foil and drying in vacuum oven. Li/ LiMn_2O_4 CR2025-coin cells were assembled with Celgard 2400 separators, electrolyte, lithium foil anode, LiMn_2O_4 cathode in the glove box, in which oxygen and water content were less than 0.1 ppm.

2.2. Electrochemical measurements and physical characterizations

Cyclic performances of LiMn_2O_4 electrode were determined by cycling coin cells at room temperature (25 °C) and elevated temperature (55 °C) on LAND system (CT2001A, Wuhan, China). Electrochemical impedance spectroscopy was performed on a PGSTAT-30 electrochemical station (Autolab, Netherland) in a frequency range of 10^5 – 10^{-2} Hz with potential amplitude of 5 mV.

For physical characterizations, the cycled cells were disassembled in the glove box. LiMn_2O_4 cathode was rinsed with anhydrous DMC for five times to remove the residual EC, EMC and LiPF_6 salt, and then dried overnight under vacuum at room temperature in glove box. The morphology of samples was observed with scanning electron microscopy (SEM, ZEISS ULTRA 55, Germany) and Transmission electron microscopy (TEM, JEM-2100HR, Japan). Surface compositions were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, U.S) and Fourier transition infrared spectroscopy (FTIR, Bruker Tensor 27, Germany) within 600–4000 cm^{-1} . The content of Mn deposited on Li foil of the cycled cell was determined by inductively coupled plasma mass spectrometry (ICP-MS) (IRIS IntrepidII XSP, U.S).

3. Results and discussion

To optimize the content of DMPP as an electrolyte additive, Li/ LiMn_2O_4 cells in the electrolytes containing various contents of DMPP were cycled under room temperature at 0.5 C for the first three cycles and at 1 C for the subsequent cycles. The obtained results are presented in Fig. 1. It can be seen that the LiMn_2O_4 electrode in base electrolyte experiences a capacity loss, from 113 mAh g^{-1} to 80.2 mAh g^{-1} after 300 cycles, showing that LiMn_2O_4 electrode in base electrolyte is instable. When DMPP is used, the capacity loss is reduced significantly, indicating that

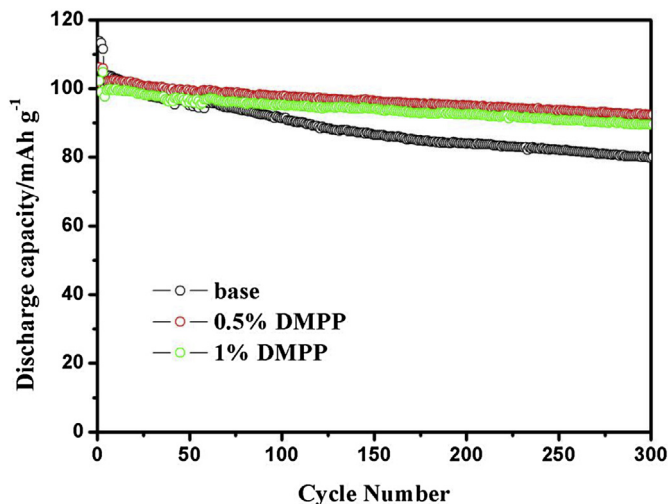


Fig. 1. Cyclic performance of LiMn_2O_4 electrode in the electrolytes containing various contents of DMPP under room temperature at 0.5 C for the first three cycles and at 1 C for the subsequent cycles between 3 V and 4.5 V.

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