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A Positive-Temperature-Coefficient Layer Based on Ni-Mixed Poly(Vinylidene Fluoride) Composites for $LiFePO_4$ Electrode

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This paper discusses a positive-temperature-coefficient (PTC) electrode prepared by coating a layer of Ni particle-mixed poly(vinylidene fluoride) (PVDF) composites between the active $LiFePO_4$ layer and current collector. The performance of the $LiFePO_4$ electrode with PTC layer is compared with the electrode without PTC layer. Experimental results from electrical resistivity, capacity, and electrochemical impedance spectrometry at different temperature demonstrate that the PTC layer shows an enormous increase of the resistance and blocks fully off electrochemical behaviors at 90 °C. These results express that the PTC layer can be used for preventing thermal runaway during the abnormal overheat. Furthermore, the rate and cycle performance at ambient temperature indicate that the PTC layer can provide favorable interface and lower electrode polarization.

Keywords: positive-temperature-coefficient; Poly(vinylidene fluoride); $LiFePO_4$ electrode; Lithium battery.

1. INTRODUCTION

Olivine $LiFePO_4$ is considered as a desirable cathode materials for Li-ion batteries due to its high theoretic specific capacity (170 mAh g^{-1}), good stability during cycling and environmental benignity [1-3].

However, safety of $LiFePO_4$ electrode is also the technical obstacle for high power demand applications. As is well known, the electrodes suffer the heat generated by chemical decomposition and chemical reactions exothermic reactions when exposed to elevated temperature [4]. If the heat output during this process exceeds the thermal diffusion, then thermal runaway occurs [5]. Therefore, it’s an attractive alternative to research thermal shutdown at high temperature. Considering this reason, commercial lithium-ion batteries are designed to add a positive temperature coefficient (PTC) resistor on the cell against external short circuit by limiting current flow when the cell temperature reaches the designed activating temperature of the device [6]. Here it should be noted that batteries regulated with external PTC devices would not only have higher manufacturing costs but also not response rapidly when hazardous reactions erupt in very high pace [6,7] at elevated temperature.

Therefore, some researchers attempt to introduce some positive-temperature-coefficient composites, which have PTC effect that electrical resistivity increases with temperature, into the internal of Lithium-ion batteries. M. Kise [8-11] reported a new safe cathode made by mixing the active materials with positive-temperature-coefficient compounds, when the cell temperature rised arising from the short circuit, overcharging and so on, resistivity of electrode can be increased drastically at higher than specified temperature (about 130 °C) and current was reduced. X. M. Feng [12] proposed a new three-layer electrode that the PTC compounds were set between the common electrode and the current collector to provide a current-limiting effect for $LiCoO_2$ electrode. L. Xia [13] devised a temperature-sensitive cathode material in which each particle was composed of a central bulk of $LiCoO_2$ and a very thin surface layer of poly(3-decylthiophene) that had an appropriate positive-temperature-coefficient (PTC) effect and this material can use as self-activating protection of lithium ion batteries. H. Zhong [14] reported two PTC electrodes based on EVA, including mixed and layered, which could protect battery at lower temperature.

However, those PTC materials consisted of carbon black/polyethylene, epoxy–carbon, poly(3-decylthiophene) and EVA are coming from external electrode, so electrode conductivity and batteries performance may be influenced. Here our idea is to choose a reagent as the PTC matrix from $LiFePO_4$ electrode, which includes active material, conductive agent and binder, to avoid needless trouble. So we consider selecting PVDF as PTC matrix, make PVDF/Ni composites as PTC compound, meanwhile set possible the transition temperature of PTC-effect as 90 °C around by controlling Ni content. Here PVDF can be also used as binder, and the layered $LiFePO_4$ electrode that PTC compound is introduced by the current collector and the $LiFePO_4$ electrode is researched. In this paper, we report a temperature-sensitive $LiFePO_4$ electrode with PTC-layer based on PVDF/Ni and evaluate the electrochemical performance of the PTC electrode at ambient temperature.

2. EXPERIMENTAL

2.1 Electrode preparation

PVDF (HSV900, $M_w = 1,000,000$), Ni particles (99.5 wt%) and Super P (particle size: 40 nm), with the mass concentration of 34%, 65%, and 1% were mixed by suitable amounts of NMP (N-methyl-2-pyrrolidone). Then mixture was combined using a Polytron PT 2500E homogenizer at 20,000 rpm for 10 min until uniform. The slurry was coated onto an aluminum collector (20 μm thickness) by a doctor blade, and dried with flowing air at 100 °C for 6 h. The PTC layer was then pressure-rolled to a predetermined thickness. Thereafter, the active material slurry which consisted of 80 wt% $LiFePO_4$ powder, 10 wt% Super P, 10 wt% PVDF was coated on this PTC layer and the laminate loading was controlled by the height of the doctor blade. The electrode was roll-pressed and finally dried at 120 °C for 6 h in vacuum. Moreover, for comparison, $LiFePO_4$ electrode without PTC layer, including same composition of active layer was made by coating the active slurry on Al foil, as reference. Both electrodes were cut into wafers with 1.0 cm diameter to be used next.

2.2 Evaluation of electrical properties

The positive-temperature-coefficient properties were evaluated by the relationship between temperature and resistivity of the $LiFePO_4$ electrode. The method was same as previous work [15] which the electrode was sandwiched between two metals electrodes by constant pressure, and the resistance was measured directly by Data Acquistion/Switch Unit (34970A, Agilent Technologies) from 20 °C to 110 °C.

2.3 Electrochemical cells

The CR2025 coin-type half cells were assembled by $LiFePO_4$ electrode (with or without electrode), a separator film (Celgard® 2400 membrane), lithium anode and filled with 70 μL of liquid electrolyte, which was 1 mol/L $LiPF_6$ dissolved in EC/DMC/EMC 1:1:1 by mass and purchased from Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd., China. All cells were fabricated in an argon-filled glove box (Universal 2440/750, Mikrouna Mech. Tech. Co., Ltd.), in which both the water content and the oxygen content were less than 1 ppm.

2.4 Evaluation of cell performance

The charge-discharge tests of $LiFePO_4$ electrode were measured between 2.5 V and 4.2 V (vs. Li/Li^+) on Land CT2001A charge/discharge instrument, China. and the cycled current was set as 0.1 C (1 C = 170 mA g^{-1}) except special purpose.

To testify directly the practical heating protect of PTC layer, both $LiFePO_4$ electrodes were designed to charge-discharge at 1 C between 2.5 V and 4.2 V at 25 °C and 90 °C.

Electrochemical impedance spectra (EIS) of the $LiFePO_4$/Li half cells was tested using PAR-STAT 2273 electrochemical measurement system (PerkinElmer Instrument, USA), and the frequency window of EIS was between 1 MHz and 0.01 Hz, with amplitude of 5 mV. In these tests, we adopted three-electrode cells, which the working electrode was $LiFePO_4$ electrode and lithium metal was used as counter and reference electrodes.

3. RESULTS AND DISCUSSION

3.1 Electrical resistivity of different electrodes

Fig. 1 shows schematic illustration of the double-layer structure and work mechanism of $LiFePO_4$ electrode with PTC layer. It's very obvious that $LiFePO_4$ electrode is consisted of $LiFePO_4$

layer, PTC layer and Al foil. Once the electrode suffers from overheating, such as short circuit or high temperature, the ohmic impedance of PTC layer increases rapidly and restrains current passing.

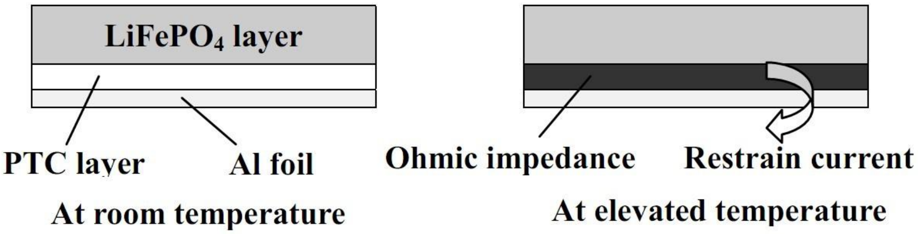

Figure 1. Schematic illustration of the double-layer structure and work mechanism

As shown in Fig. 2, resistivity of the two electrodes at different temperature is studied. Clear seen that there is no resistivity change for $LiFePO_4$ electrode without PTC layer from 10 °C to 105 °C. Resistivity of PTC electrode keeps constant below 80 °C as same as the tendency of blank electrode, and rises slightly between 80 °C to 90 °C, but when temperature exceeds 90 °C, the impedance increases several tens of times than that of ambient temperature (25 °C). It can be explained that the increasing of PTC-electrode resistivity is caused by the PTC layer which included PTC compound based on PVDF/Ni is highly sensitive to high temperature as M. Kise reported [8]. The increasing trend of PVDF/Ni layer is similar to A. Kono [16] work that PVDF/Ni composites has nice PTC effect and the transition temperature is below 100 °C with 30 vol.% Ni content. It's well known that when the temperature of electrodes exceeds 100 °C, many side reactions will happen, such as decomposition of SEI, solvent evaporation, and oxidation reaction between the cathode and the electrolyte [13] and the safety is uncertain. Therefore it's certainly essential to shut down those adverse reactions at lower temperature and the PTC layer provides suitable convenience of current-limiting effect.

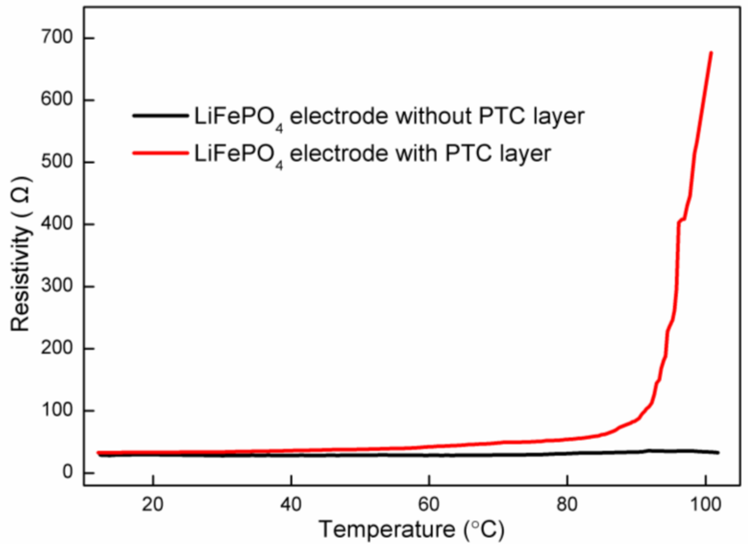

Figure 2. The relationship between temperature and resistivity of the $LiFePO_4$ electrode with or without PTC layer

3.2 The capacity of $LiFePO_4$ electrodes at different temperature

Fig. 3 shows the capacity curves of different $LiFePO_4$ electrodes at 1 C between 2.5 V and 4.2 V at different temperature. From Fig. 3a and Fig. 3b, it is obvious that when temperature reaches 90 °C from 25 °C, $LiFePO_4$ electrode with PTC layer cannot discharge in contrast that $LiFePO_4$ electrode without PTC layer can normally discharge. After observing scrutinizingly Fig. 3a, it can be discovered that discharge capacity of $LiFePO_4$ electrode with PTC layer is 141.4 mAh g^{-1}, higher than 132.7 mAh g^{-1} observed in $LiFePO_4$ electrode without PTC layer. Moreover, $LiFePO_4$ electrode with PTC layer shows a lower charge plateau potential and a higher discharge plateau potential than that of without PTC layer. The discharge plateau potential for $LiFePO_4$ electrode with PTC layer is 3.40 V, while it is 3.38 V for $LiFePO_4$ electrode without PTC layer. Besides, the charge plateau potential is 3.46 V for $LiFePO_4$ electrode with PTC layer, which is about 0.01 V lower than 3.47 V for $LiFePO_4$ electrode without PTC layer. The smaller potential separation between the charge and discharge plateaus indicates better kinetics characteristics and better reversibility of $LiFePO_4$ electrode with PTC layer, which can be ascribed to the lower potential polarization of the electrode during the charge and discharge processes. However, when the temperature touches 90 °C, shown in Fig. 3b, discharge capacity of $LiFePO_4$ electrode without PTC layer is 135.9 mAh g^{-1}, which is higher than the capacity at ambient temperature (132.7 mAh g^{-1}, shown in Fig. 3a) explained that faster Li^+ diffusion at high temperature[14]. Whereas it's very evident seen that discharge capacity of $LiFePO_4$ electrode with PTC layer is only 0.6 mAh g^{-1}, near to zero, led by which the serious ohmic polarization of PTC effect at 90 °C restricts fully discharge of $LiFePO_4$ electrode. Thus the PTC layer can provide favorable reversibility for $LiFePO_4$ electrode at room temperature and be an effective pattern for preventing thermal runaway by this sensitivity of resistance to temperature at high temperature.

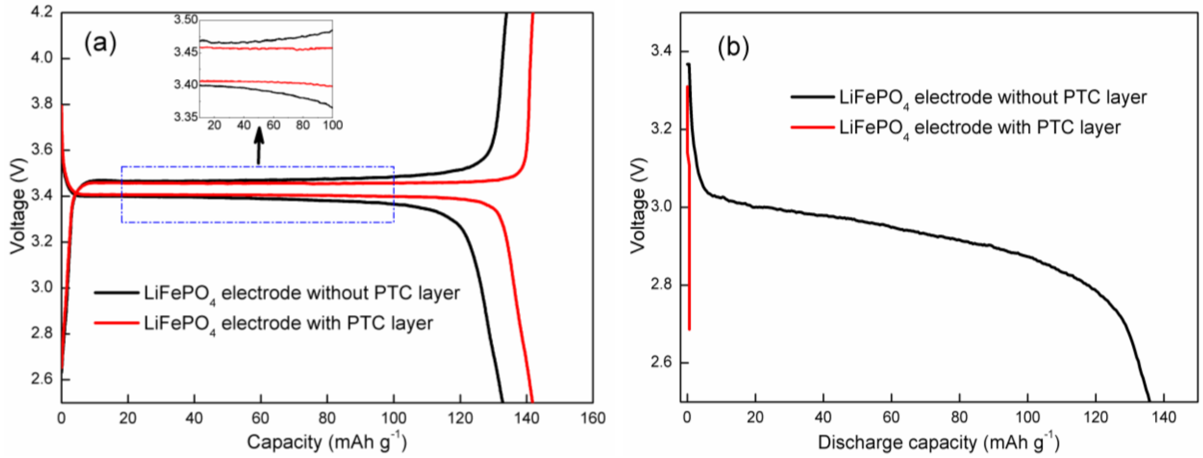

Figure 3. The capacity curves of the $LiFePO_4$ electrode with or without PTC layer at 1 C between 2.5 V and 4.2 V at different temperature: (a) charge-discharge capacity at 25 °C; (b) discharge capacity at 90 °C.

3.3 Electrochemical impedance spectroscopy

To evidence commendably the influence of PTC layer on the electrochemical behavior of $LiFePO_4$ electrode, EIS was applied to the cells at different temperature. Fig. 4 shows EIS plots of different $LiFePO_4$ electrodes at 25 °C, 80 °C, 90 °C. As similar to previous work [12,17], the semicircle of impedance curve at high frequencies represents charge transfer resistance (R_{ct}). Seen Fig. 4a, it's very distinct that R_{ct} is raising expeditiously along with temperature, especially at 90 °C. Calculated approximately from this spectra, R_{ct} of $LiFePO_4$ electrode with PTC layer at 25 °C, 80 °C, 90 °C is respective around 270 Ω, 360 Ω, 820 Ω. The increasing trend of impedance can be explained that the aggrandizement of electrode resistivity leads immediately to inhibiting R_{ct}. Caused by the resistivity slightly increasing from 25 °C to 80 °C, R_{ct}-rate of grown is not very large. However, when temperature reaches 90 °C, R_{ct} grows over triple than 25 °C, accordant comparatively with expeditious electrode resistance. In contrast, R_{ct} of $LiFePO_4$ electrode without PTC layer is appeared to decline lentamente shown in Fig. 4b, separately 320 Ω at 25 °C, 250 Ω at 80 °C, 240 Ω at 90 °C. This decrease is brought about by the increase in ionic conductivity of the electrolyte [10]. Therefore, the data in Fig. 4 demonstrates that the PTC layer can hinder charge transfer by raising its resistance and then suppress efficaciously electrochemical reactions at overheat conditions.

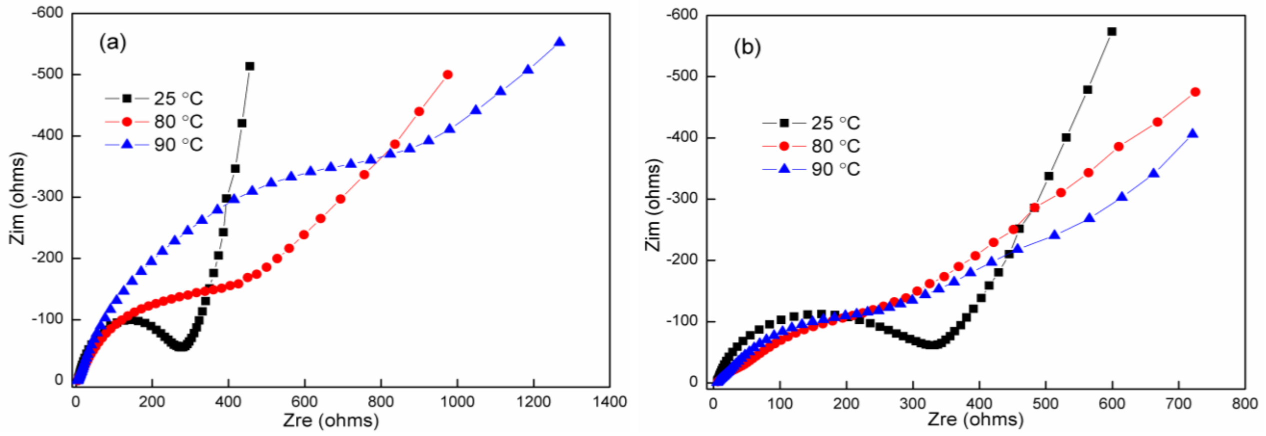

Figure 4. Nyquist plots of different $LiFePO_4$ electrodes at 25 °C, 80 °C, 90 °C: (a) $LiFePO_4$ electrode with PTC layer; (b) $LiFePO_4$ electrode without PTC layer.

3.4 The performance of $LiFePO_4$ electrode at room temperature

Fig. 5 shows discharge capacity of $LiFePO_4$ electrode with or without PTC layer at different current. It's clear seen that discharge capacity of $LiFePO_4$ electrode with PTC layer is obviously higher than that of without PTC layer at all rates and the higher capacity is around 2 mAh g^{-1} at 0.1 C, 3 mAh g^{-1} at 0.3 C, 7 mAh g^{-1} 0.5 C, 10 mAh g^{-1} at 1.0 C, 11 mAh g^{-1} at 1.5 C and 15 mAh g^{-1} at 2 C, meanwhile gap of capacity between different $LiFePO_4$ electrodes increases with the rate. The trends seen in the rate data are found to correlate well with the charge-transfer resistance determined by EIS analysis between different electrodes at 25 °C which the $LiFePO_4$ electrode without PTC layer exhibits larger R_{ct} (325 Ω) than that of with PTC layer (275 Ω) from Fig. 3. As the active layers and current collector in these electrodes are same, the observed difference in the charge-transfer resistance is apparently associated with the contact between two layers.

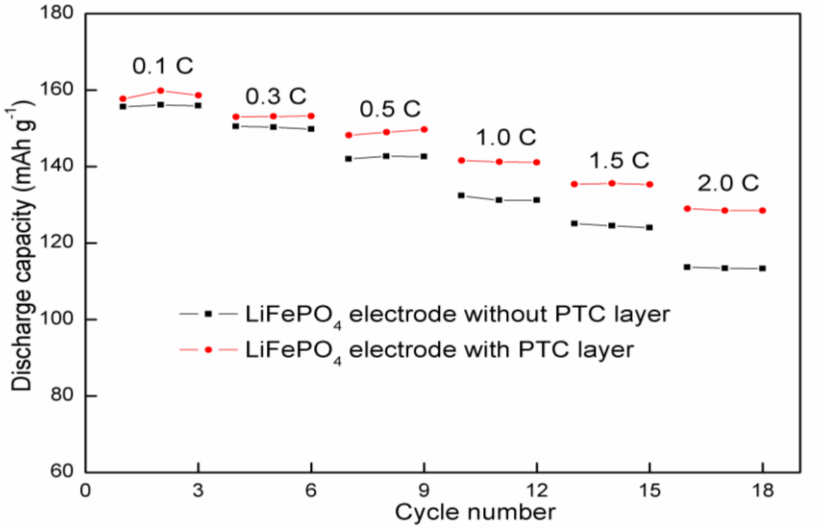

Figure 5. Discharge capacity of the $LiFePO_4$ electrode with or without PTC layer at different rates

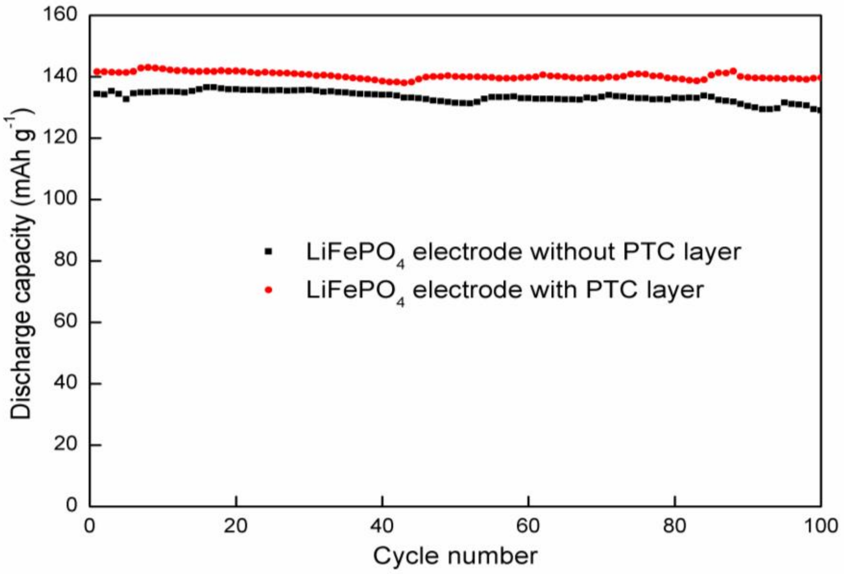

Figure 6. Cycle life test of the $LiFePO_4$ electrode with or without PTC layer at 1 C rate

Thereby this sandwiched layer can shorten availably interface resistance and improve the power performance. Enhancement in power performance of $LiFePO_4$ electrode is homologous with K. Striebel report [18] by placing a PVDF-bound C black layer between Al current collector and a $LiFePO_4$ overlay. The cycle stability of the electrode is also found to show strong dependence on the PTC layer. Fig. 6 presents cycle performance of $LiFePO_4$ electrode with or without PTC layer at 1C current density between 2.5 V and 4.2 V. It can be seen that $LiFePO_4$ electrode with PTC layer shows better cycle stability than that of without PTC layer. The discharge capacity of $LiFePO_4$ electrode without PTC layer is 134.4 mAh g^{-1} for the initial cycle and decreases to 129 mAh g^{-1} after 100 cycles with capacity retention ratio of 95.98%, which is similar to others result [19-21]. Whereas the discharge capacity of $LiFePO_4$ electrode with PTC layer is 141.6 mAh g^{-1} for initial cycle and high reversible capacity of 139.7 mAh g^{-1} is retained after 100 cycles with capacity retention ratio of 98.66%, which indicates that electrode with PTC layer can deliver 100 cycles with lower capacity fading at the current density of 1 C, showing a great improvement in cyclability, which can be owed to favorable interface and showing lower electrode polarization.

4. CONCLUSIONS

In this paper, we develop a PTC layer electrode by coating PVDF/Ni composites between $LiFePO_4$ electrode and Al foil. The experimental results reveal that the resistivity and the charge transfer resistance increase rapidly, the capacity is shut absolutely down at the temperature over 90 °C, which can obviously be used for self-actuating thermal cut-off of $LiFePO_4$ electrode. Meanwhile the rate and cycle performance of $LiFePO_4$ electrode are improved largely attributed to favorable interface and lower electrode polarization supplied by the PTC layer. Therefore, we conclude that the PTC layer can improve the safety and power performance of $LiFePO_4$ electrode and hope that the PVDF/Ni-PTC layer could be applied to more active materials, not only $LiFePO_4$.

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