

Effect of an inorganic additive on cycling performance of Li/V₂O₅ polymer cells prepared with gel polymer electrolyte

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Abstract

A gel polymer electrolyte is prepared by soaking a polymer-coated separator in electrolyte solution that contains an inorganic additive. The porous polymer coated on the separator is gelled by soaking in an electrolyte solution to encapsulate a larger amount of electrolyte solution. By using the gel polymer electrolyte, lithium-metal-polymer cells composed of a lithium anode and V₂O₅ cathode are assembled and their cycling performances are evaluated. The effect of an inorganic additive (AlI₃) on the cycling performance of Li/V₂O₅ polymer cells is investigated. The addition of AlI₃ to the gel polymer electrolyte reduces the interfacial resistance and thus the cells exhibit a less capacity fading and better high rate performance.

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1. Introduction

Rechargeable lithium batteries employing lithium metal as an anode are most attractive candidates for power sources with high specific energy for portable electronic devices, electric vehicles and load-levelling systems. The major problem that prevents the successful development of lithium-metal batteries is the risk associated with the reactivity of lithium metal that can affect the cycle-life and safety of the batteries. In order to solve this problem, many researchers have tried to modify the chemical properties of the interface formed on the lithium electrode. For example, the selection of solvents and salts compatible with lithium metal has been reported [1] and addition of inorganic, organic, surfactant and gaseous additives to electrolytes have focused mainly on the chemical modification of a lithium surface [2–8]. Ishikawa et al. [9,10] have re-

ported that a Li–Al alloy layer formed on a lithium anode by inorganic additives such as aluminum iodide (AlI₃) suppresses the dendritic deposition of lithium and enhances the cycling efficiency. It is also widely known that the dendritic growth of lithium can be suppressed by applying a gel polymer electrolyte to lithium-metal batteries [11].

This study reports the cycling performances of lithium-metal-polymer cells composed of a metallic lithium anode, a gel polymer electrolyte containing an inorganic additive and a vanadium pentoxide (V₂O₅) cathode. By using the gel polymer electrolyte, the electrolyte solution does not get leaked from the cell and the electrolyte can be prepared as a thin film, which allow the cells to be packaged in plastic material. To prevent dendritic growth of the lithium electrode during charge–discharge cycling, a small amount of aluminum iodide is added to the gel polymer electrolyte. Vanadium pentoxide is used as a cathode because it is easy to synthesize, has acceptable production, costs and exhibits a large lithium-insertion capacity [12–14].

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2. Experimental

2.1. Preparation of gel polymer electrolyte and electrodes

The gel polymer electrolyte was prepared from a porous polymer-coated separator, as previously reported [15]. The gellable polymer coated on the polyethylene (PE) separator was an acrylonitrile (AN)–methyl methacrylate (MMA) random copolymer (hereafter called the AM copolymer). The molar ratio of AN and MMA in the AM copolymer was 84:16. To prepare the polymer-coated separator, the AM copolymer was dissolved in anhydrous dimethylformamide (DMF). A microporous PE separator (Asahi Kasei, thickness: 25 μm) was then immersed in the polymer solution for 3 h. The separator was taken out and immersed in a water bath for 5 h to induce phase inversion. The resulting polymer-coated separator was washed with deionized water and vacuum dried at 80 $^{\circ}\text{C}$ for 24 h. The gel polymer electrolyte was prepared by soaking the polymer-coated separator in 1 M LiClO_4 in ethylene carbonate (EC)/propylene carbonate (PC) (1:1 by volume, Samsung Cheil Industries, battery grade) for 1 h. Anhydrous AlI_3 (Aldrich, 99.999%) was added to the electrolyte solution at a concentration of 500 ppm. For the purpose of making the cathode, 85 wt.% crystalline V_2O_5 , 10 wt.% super-P carbon and 5 wt.% poly(vinylidene fluoride) were mixed in *n*-methyl pyrrolidinone to form a homogeneous paste, which was then coated on an aluminum foil. The cathode was roll-pressed to enhance the contact and adhesion of the particulate to foil. The thickness of the V_2O_5 cathode was about 25 μm after roll-pressing and its loading of active mass corresponded to a capacity of about 1.2 mAh cm^{-2} . The anode consisted of a lithium foil of 50- μm thickness (Cyprus Foote Mineral Co.) that was pressed on to a copper current-collector.

2.2. Electrical measurements

The gel polymer electrolyte was sandwiched between two stainless-steel (SS) electrodes for conductivity measurements. The a.c. impedance measurements were performed by means of a Zahner Elektrik IM6 impedance analyzer. Cyclic voltammetry was performed on a V_2O_5 working electrode, with counter and reference electrodes of lithium, at a scanning rate of 0.1 mV s^{-1} . Each $\text{Li}/\text{V}_2\text{O}_5$ polymer cell was assembled by sandwiching the gel polymer electrolyte between a lithium anode and a V_2O_5 cathode. The cell was then enclosed in a metallized plastic bag and vacuum-sealed. All assembly of the cells was carried out in a dry box that was filled with argon gas. Charge and discharge cycling tests of the $\text{Li}/\text{V}_2\text{O}_5$ polymer cell were conducted over a voltage range of 2.0–4.0 V with Toyo battery-test equipment (TOSCAT-3000U). To measure the discharge capacities at low temperature, the cells were charged at the 0.2 C rate at room temperature, equilibrated at the test temperature for 6 h and then discharged at a constant current of 0.2 C.

3. Results and discussion

As the AM copolymer was coated on the PE separator by dip coating and phase inversion, micropores were formed and the distribution of pores was observed to be uniform, as reported previously [15]. The presence of micropores on the surface of the polymer-coated separator can lead to efficient uptake of the liquid electrolyte when it is soaked in an electrolyte solution, which finally results in gelation of the coated polymer. Since some of the AM copolymer penetrated into the pores of PE separator, the coated polymer could be physically affixed to the PE separator. The thickness of polymer layer coated on both sides of the PE separator was about 7 μm . The polymer-coated separator was soaked in LiClO_4 –EC/PC containing AlI_3 for 1 h. The polymer on both sides of PE separator was gelled in contact with the electrolyte solution. The ionic conductivity after soaking in the electrolyte solution was $7.6 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. The polymer layer became very sticky after the physical gelation and was thus expected to promote a strong interfacial adhesion between the electrodes. Linear sweep voltammetry of the gel polymer electrolyte shows the onset of current above 5.0 V versus Li. This can be assigned to the decomposition voltage of the gel polymer electrolyte.

Cyclic voltammograms of a $\text{Li}/\text{V}_2\text{O}_5$ polymer cell for Li intercalation (reduction) and deintercalation (oxidation) are shown in Fig. 1. The positive currents are for oxidation (charge) and the negative currents for reduction (discharge). The electrolyte solution used in preparing the gel polymer electrolyte was LiClO_4 –EC/PC with and without AlI_3 . On scanning the V_2O_5 electrode in a negative direction, the main cathodic peaks are observed at 3.28, 3.09 and 2.16 V and correspond to the intercalation of lithium ions into the V_2O_5 electrode. On the reverse scan, oxidation peaks are observed at 2.62, 3.39 and 3.49 V and are associated with the de-intercalation of lithium ions from the $\text{Li}_x\text{V}_2\text{O}_5$. The potentials for the peak current are almost the same in the both cells, regardless of addition of AlI_3 . The peak currents are, however, higher in the cell prepared with LiClO_4 –EC/PC containing AlI_3 , which means that the internal resistance of the cell is decreased when adding AlI_3 to the gel polymer electrolyte. The peak currents decrease slightly and stabilize after the third cycle, which confirms the reversibility of the electrochemical reaction.

In order to investigate the effect of AlI_3 on the interfacial behaviour of the $\text{Li}/\text{V}_2\text{O}_5$ polymer cell, measurements were made of the a.c. impedance of cells prepared using gel polymer electrolyte with and without AlI_3 . The a.c. impedance spectra before and after the cyclic voltammetric measurements are shown in Fig. 2. Although the resistance includes contributions from both the cathode and the anode in the cell, the major contribution comes from of the resistance of the anode solid electrolyte interphase (SEI) [16,17]. Since the equivalent circuit for the SEI is extremely complex and has to be represented by a very large number of series and parallel distributions of RC elements, a rigorous identifica-

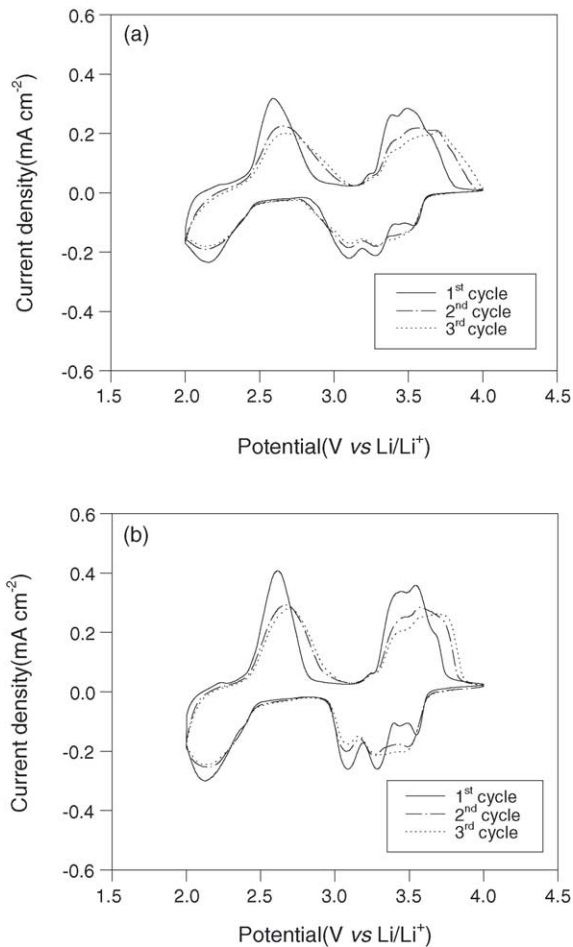


Fig. 1. Cyclic voltammograms for $\text{Li}/\text{V}_2\text{O}_5$ polymer cells prepared with and without AlI_3 . Scan rate is 0.1 mV s^{-1} and potential is taken between 2.0 and 4.0 V: (a) without AlI_3 and (b) with AlI_3 .

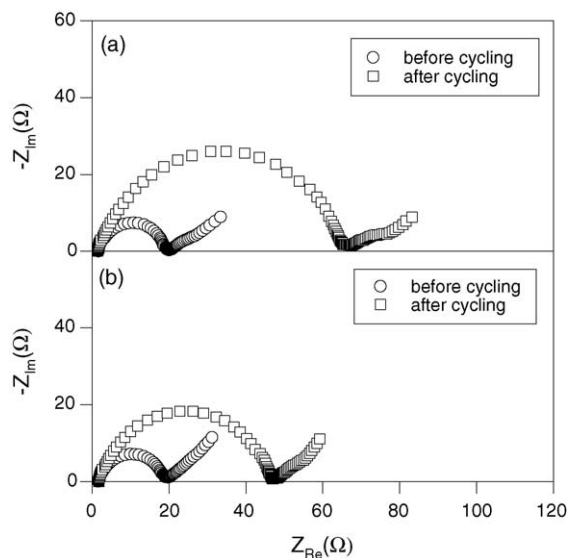


Fig. 2. The a.c. impedance spectra of $\text{Li}/\text{V}_2\text{O}_5$ polymer cells before and after cyclic voltammetric measurements: (a) without AlI_3 and (b) with AlI_3 .

tion of a combination of many poorly separated semicircles is beyond the scope of this work. Of particular interest in the a.c. impedance spectra is the total interfacial resistance. For the freshly-made cells, the value of interfacial resistance is almost same in the absence and the presence of AlI_3 . After repeated cycling, the interfacial resistance is increased in the both cells. After three cycles, the interfacial resistance in the cell prepared with $\text{LiClO}_4\text{-EC/PC}$ containing AlI_3 is lower than that in the cell prepared without AlI_3 . In the gel polymer electrolyte containing EC/PC without AlI_3 , passivation occurs with a continuous growth and with a cumulative trend. Aprotic solvents such as EC and PC are well known to form a resistive passivating layer on lithium metal [18–20]. On the other hand, in the gel polymer electrolyte containing EC/PC with AlI_3 , Al^{3+} ions dissolved in the gel polymer electrolyte can form a thin layer of Li–Al alloy on the electrode surface during cathodic deposition of Li and the resulting Li–alloy film with high conductivity will reduce the charge-transfer resistance. The formation of a Li–Al alloy in the presence of AlI_3 has been reported by other workers [2,9,10]. Furthermore, the reaction between the iodide anion and lithium on the electrode may form a conductive LiI layer on the lithium electrode, which also reduces the interfacial resistance.

The charge–discharge curves (0.1 C rate) of $\text{Li}/\text{V}_2\text{O}_5$ polymer cell using a gel polymer electrolyte prepared with $\text{LiClO}_4\text{-EC/PC}$ containing AlI_3 , are shown in Fig. 3. Comparison of the cyclic voltammograms (Fig. 1) and the charge–discharge curves (Fig. 3) demonstrates that there is a strong correlation between the potentials for peaks in the cyclic voltammogram and the plateaux in the charge–discharge curve. The first two plateaux at 3.3 and 3.1 V during the first discharge cycle are associated with the formation of LiV_2O_5 and correspond to a one-electron reduction. There is an additional plateau at 2.2 V and this corresponds to further reduction of the cathode to form $\text{Li}_2\text{V}_2\text{O}_5$. The theoretical capacity is estimated to be 295 mAh g^{-1} based on V_2O_5 when two Li^+ ions per

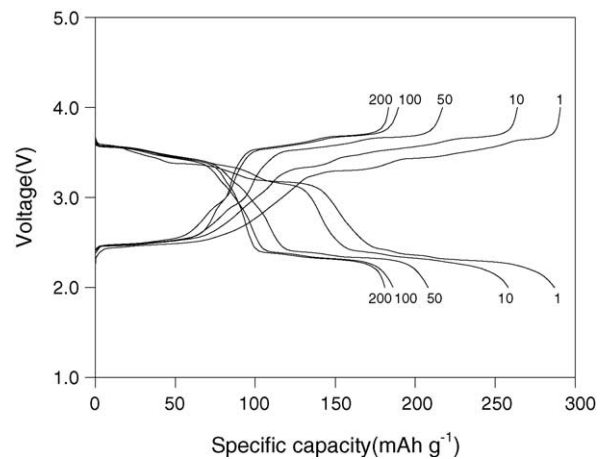


Fig. 3. Charge and discharge curves (1, 10, 50, 100 and 200 cycles) of $\text{Li}/\text{V}_2\text{O}_5$ polymer cell using gel polymer electrolyte prepared with $\text{LiClO}_4\text{-EC/PC}$ containing AlI_3 , 0.1 C rate.

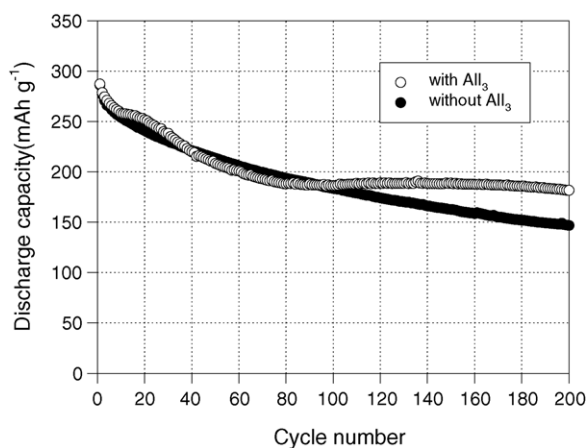


Fig. 4. Discharge capacity as a function of cycle number for Li/V₂O₅ polymer cells prepared with and without AlI₃. Cycling conducted out at a constant current density of 0.12 mA cm⁻² between 2.0 and 4.0 V.

V₂O₅ are incorporated. As can be seen in Fig. 3, the cell has an initial discharge capacity of 287 mAh g⁻¹, which corresponds to a utilization of 97% based on two equivalents of lithium per mol of V₂O₅. During the following charge of the cell, most of the lithium ions are de-intercalated, i.e., the charge capacity is almost same to the discharge capacity.

The discharge capacities are shown in Fig. 4 as a function of cycle number for Li/V₂O₅ polymer cells prepared with and without AlI₃. The discharge capacity slowly decreases with cycling in the both cells, which is probably due to an increase in the cell resistance. The cycling characteristics of the Li/V₂O₅ polymer cell are little influenced by the presence of AlI₃ during the first 100 cycles. After 100 cycles, the Li/V₂O₅ polymer cell containing AlI₃ exhibits more stable cycling characteristics than those of the Li/V₂O₅ polymer cell without AlI₃. As discussed earlier, the formation of a Li–Al alloy and LiI on the lithium electrode in the presence of AlI₃ could give better capacity retention during repeated cycling, because such surface films provide the lithium electrode with good stability towards reduction of the electrolyte. The decline in capacity is about 0.24 and 0.18% per cycle, in the absence and presence of AlI₃, respectively (see Fig. 4).

The a.c. impedance spectra of a Li/V₂O₅ polymer cell on repeated cycling, are shown in Fig. 5. The spectra, obtained at a fully charged state reveal that the low-frequency semi-circle expands with repeated cycling up to 100th cycle in the both cells, which indicates an increase in the interfacial resistance. An increase of interfacial resistance is related to both the continuous growth of a passivation layer on the lithium anode and the deterioration of the interfacial contacts at the cathode. The latter process results from the change in the lattice of the V₂O₅ active material during cycling. It should be noted that the interfacial resistance decreases after the 100th cycle in the Li/V₂O₅ polymer cell that contains AlI₃. It is plausible that lithium-ion transport through the SEI is easier after repeated cycling, because a highly conductive SEI film is formed in the presence of AlI₃. A thin layer of Li–Al alloy

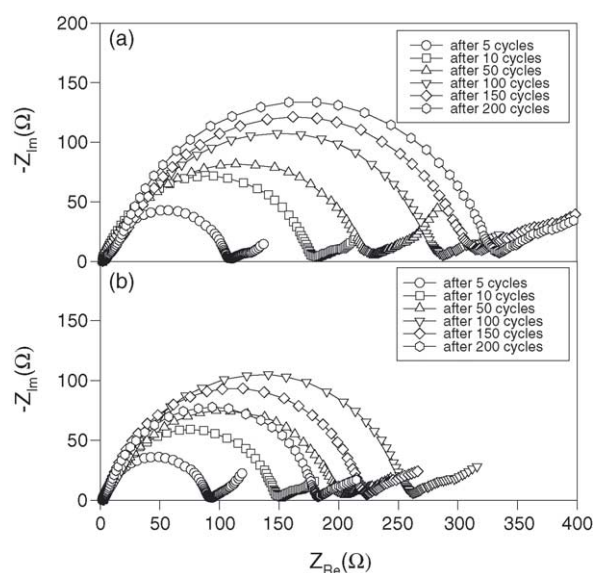


Fig. 5. The a.c. impedance spectra for Li/V₂O₅ polymer cells prepared with and without AlI₃, which are measured after repeated cycling: (a) without AlI₃ and (b) with AlI₃.

formed on the lithium anode will also increase the uniformity of the lithium electrode and thus reduces the charge-transfer resistance. Therefore, it can be concluded that the stable cycling characteristics of the Li/V₂O₅ polymer cell containing AlI₃ can be ascribed to the formation of a conductive SEI and an efficient charge-transfer reaction.

The rate capability of a Li/V₂O₅ polymer cell prepared with LiClO₄–EC/PC and AlI₃ was evaluated. The discharge curves obtained at different current rates are given in Fig. 6. For comparison, the discharge profiles for a Li/V₂O₅ polymer cell without AlI₃ are also shown. The charge current was 0.12 mA cm⁻² (0.1 C) for all measurements. The discharge capacities are almost the same for both cells at low current density (0.05, 0.1 and 0.2 C), regardless of the addition of AlI₃. This may be due to the fact that the chosen current rates are not sufficiently high to reflect the difference in the interfacial resistances. On increasing the current rate from 0.5 to 1.0 C, however, the cell prepared with gel polymer electrolyte containing AlI₃ not only shows lower polarization but also delivers a higher discharge capacity. The high-rate performance of the cell prepared with gel polymer electrolyte containing AlI₃ is likely encouraged by the fast kinetics of the charge-transfer reaction and a less resistive SEI film on the lithium anode, as already discussed.

The low-temperature performance of a Li/V₂O₅ polymer cell prepared with LiClO₄–EC/PC containing AlI₃ was evaluated. The discharge curves obtained at different temperatures are given in Fig. 7. The relative capacity is defined as the ratio of the discharge capacity at the test temperature to that delivered at room temperature. Both the voltage and the capacity decrease gradually with decreasing temperature. This results from the high polarization due to the increase in the internal resistance of the cell and from reduced lithium-ion diffusivity

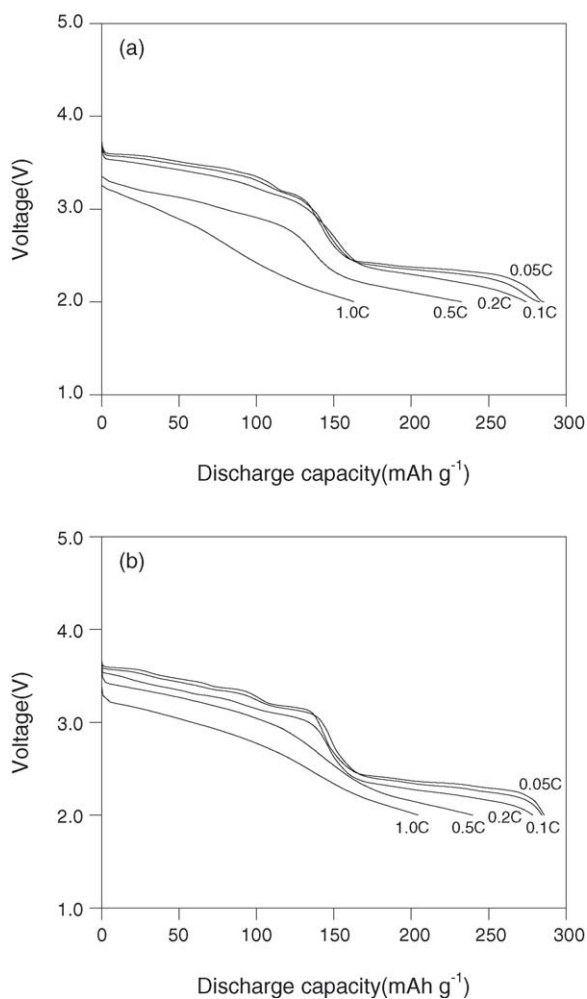


Fig. 6. Discharge profiles for Li/V₂O₅ polymer cells at different current rates: (a) without AlI₃; (b) with AlI₃.

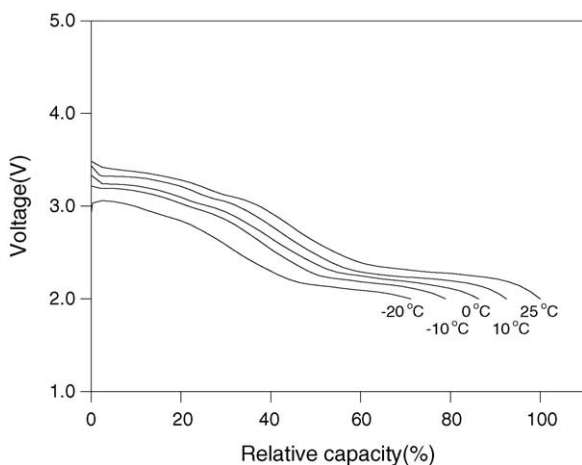


Fig. 7. Discharge profiles for Li/V₂O₅ polymer cell containing AlI₃, at different temperatures. Charge rate 0.2C with 4.0V cut-off at room temperature; discharge rate 0.2C with 2.0V cut-off at test temperature.

in the electrode. The cell resistance includes both the electrolyte resistance and the interfacial resistance. At -20°C , the discharge capacity of the cell is 71% of that delivered at room temperature. The good performance at room temperature is related to the use of an organic solvent with a low freezing point and to the formation of a highly conductive SEI layer on the lithium electrode.

4. Conclusions

A gel polymer electrolyte is prepared by soaking a polymer-coated separator in LiClO₄-EC/PC containing AlI₃. The ionic conductivity and the electrochemical stability window of the gel polymer electrolyte are $7.6 \times 10^{-4} \text{ S cm}^{-1}$ and 5.0 V versus Li/Li⁺, respectively. Lithium-metal-polymer cells composed of a lithium anode and a V₂O₅ cathode deliver a high initial discharge capacity of 287 mAh g⁻¹ based on the active V₂O₅ material. The cycling performance of Li/V₂O₅ polymer cells is improved by the addition of AlI₃. During the cathodic deposition of lithium, the Al³⁺ ions in the gel polymer electrolyte form a thin layer of Li-Al alloy, which reduces the interfacial resistance. Li/V₂O₅ polymer cells containing AlI₃ as an additive show good capacity retention with cycling, an attractive discharge capacity of 204 mAh g⁻¹ at the 1.0C rate and a good low-temperature performance, namely 71% of the room temperature capacity at -20°C .

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