

Thermal stability of lithium anodes in an amorphous V_2O_5/Li battery system

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Abstract

Safety is one of the most important factors in the development of lithium cells. The thermal stability of $a\text{-}V_2O_5/Li$ cells is investigated. Vanadium compound deposition on a lithium anode during charge/discharge cycles is observed. Vanadium compounds dissolve electrochemically and are deposited on the anode. The low reactivity of the vanadium deposited lithium anode is observed by calorimetry. Chemical-state analysis and morphological investigation of the lithium anode suggest that the improvement in stability is primarily due to the passivation film.

Introduction

Lithium cells that use amorphous V_2O_5 ($a\text{-}V_2O_5$) as the cathode active material [1] are one of the most promising types of cell in terms of capacity and cycleability. Safety, however, must also be considered in the development of Li cells. For customer use, Li secondary cells must be developed that do not vent with fire as the result of thermal or electrical abuse.

Wilkinson *et al.* [2] recently reported that the thermal stability of Li cells tends to decrease as the number of charge/discharge cycles increases. This tendency is explained by the increase in the surface area of the Li anode during charge/discharge cycles, since heat generation leading to thermal runaway can be caused by the reaction of metallic Li with the electrolyte [2, 3].

This paper reports an improvement in thermal stability in $a\text{-}V_2O_5/Li$ cells. The cause of the improvement is also discussed in terms of the anode morphology and the features of the passivation film.

Experimental

Coin-type cells (23 mm in diameter and 2 mm thick) were made using $a\text{-}V_2O_5$ as the cathode active material and $LiAsF_6$ /ethylene carbonate (EC)-2-methyl-tetrahydrofuran (2-MeTHF) as the organic electrolyte [4]. After several charge/discharge cycles, the coin-type cells were disassembled. The elements deposited on the Li anodes were analyzed with an inductively-coupled plasma atomic emission spectrometer.

The valency of the chemical species deposited on the Li anodes was analyzed with an X-ray photoelectron spectrometer (XPS).

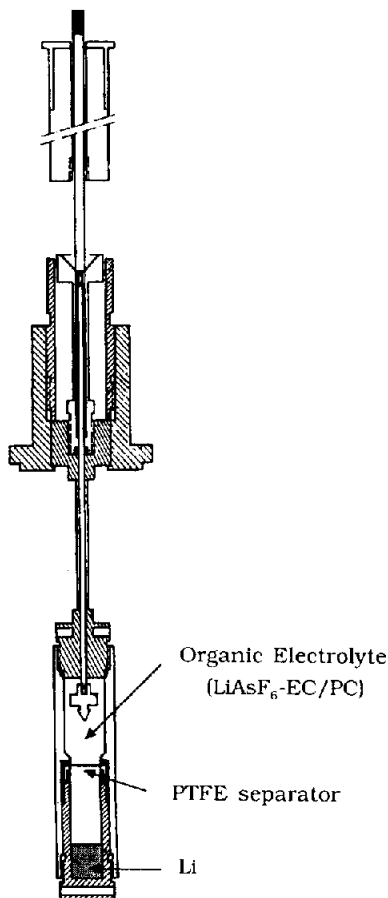


Fig. 1. Configuration of sample cell for calorimetry.

The morphology of the Li anodes was observed with a scanning electron microscope (SEM) [5].

The reaction heat between the Li and the electrolyte was measured with a SETARAM C80 calorimeter. Figure 1 shows the configuration of a sample cell. The cells were separated into two sections with a polytetrafluoroethylene (PTFE) film. The upper section contained organic electrolyte (LiAsF₆/EC-propylene carbonate (PC)) and the lower section contained Li deposited on 0.01 mm thick stainless steel (3.73×10^{-4} mol). The PTFE separator was breached at several temperatures (100–180 °C), and the reaction heat between the Li and the electrolyte was measured.

Results and discussion

Vanadium was a main element deposited on the Li anode in a-V₂O₅/Li cells. The amount of deposited vanadium increased with the accumulation capacity, as shown in Fig. 2. No vanadium compounds were deposited in fresh cells. The amount of

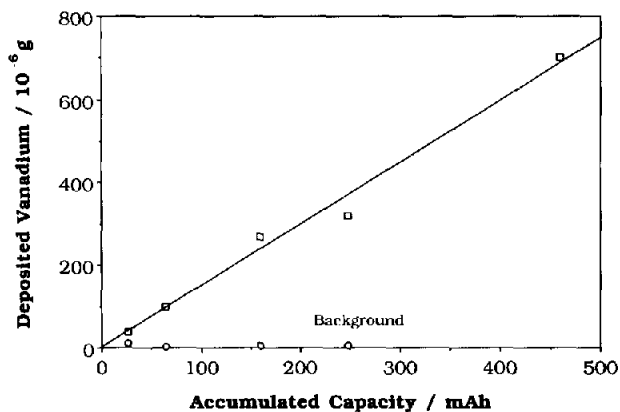


Fig. 2. Vanadium deposition vs. accumulation capacity.

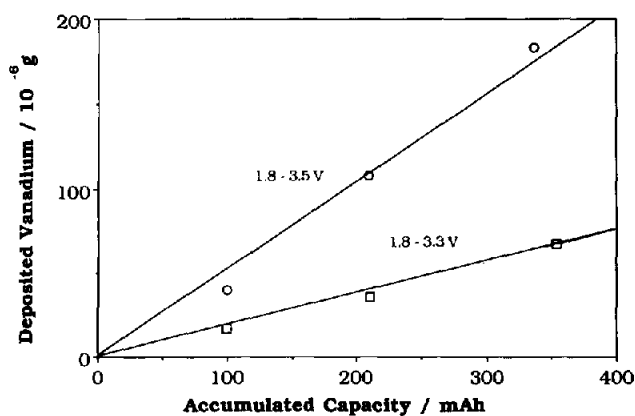


Fig. 3. Vanadium deposition vs. upper voltage limit.

vanadium compound deposited also depends on the upper cycle voltage limit as shown in Fig. 3. A greater increase in vanadium deposition was observed when cells were cycled between 1.8 and 3.5 V than in cells cycled between 1.8 and 3.3 V. Therefore, vanadium compounds will dissolve electrochemically from Li-intercalated α - V_2O_5 cathodes and be deposited on the anodes.

The vanadium compounds deposited on the Li anodes were investigated using XPS. Broad $V2p_{3/2}$ peaks were observed as shown in Fig. 4. This shows that the oxidation number of the deposited vanadium ranged from V(III) to V(V). Vanadium compounds deposited on the anodes may react with Li to form several oxidation states.

The reactivity of the vanadium-deposited Li was investigated precisely with a calorimeter. Two types of deposited Li were prepared. One was deposited from precycled $LiAsF_6/EC-2-MeTHF$ in an α - V_2O_5/Li test cell. The precycled organic electrolyte contained vanadium compounds. Deposited Li from the organic electrolyte then contained vanadium compounds. The amount of vanadium compound on the deposited Li was around 1.3×10^{-8} mol. The other type was deposited from pure $LiAsF_6/EC-2-MeTHF$. This Li was regarded as pure Li containing no vanadium

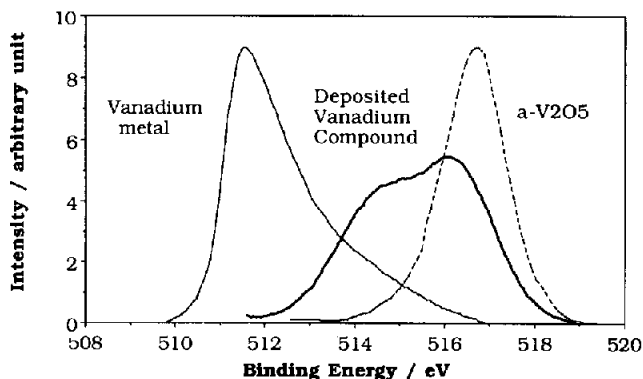


Fig. 4. X-ray photoelectron spectra of vanadium deposited on lithium anode.

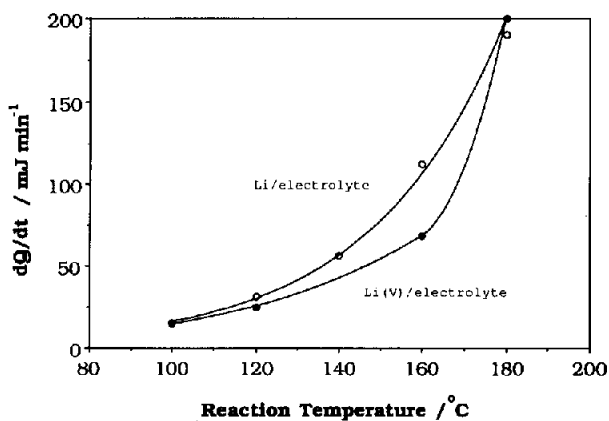


Fig. 5. Influence of vanadium deposition on reactivity in lithium anode.

compounds, although there may be products from the reaction of Li with the organic electrolyte. The heat of the reaction between the vanadium-deposited Li and the electrolyte was lower than that of pure Li in the region below 180 °C, as shown in Fig. 5. The passivation of the reaction by vanadium deposition may be one of the reasons for the thermal stability improvement in the a-V₂O₅/Li cell [6]. The reaction heat of the two samples, however, was almost same at 180 °C, which may be related to the melting point of Li (179 °C). Namely, passivation of the reaction is only effective below the melting point of Li. These results suggest that vanadium compounds may alter the features of passivation films or the morphology of the Li anode.

Figure 6 shows Cole-Cole plots of a-V₂O₅/Li cells which were cycled until about 100 mA h of their accumulated capacity. One cell was cycled between 1.8 and 3.3 V. The other was cycled between 1.8 and 3.5 V. Figure 6 suggests that vanadium deposition changes the characteristics of passivation film.

The morphological change in the Li anode caused by vanadium deposition was also investigated. Two types of cycle were used for the a-V₂O₅/Li cells. One cell was charged to 3.3 V and the other was charged to 3.5 V with the same discharge capacity. A greater amount vanadium compound was deposited in the latter than in the former.

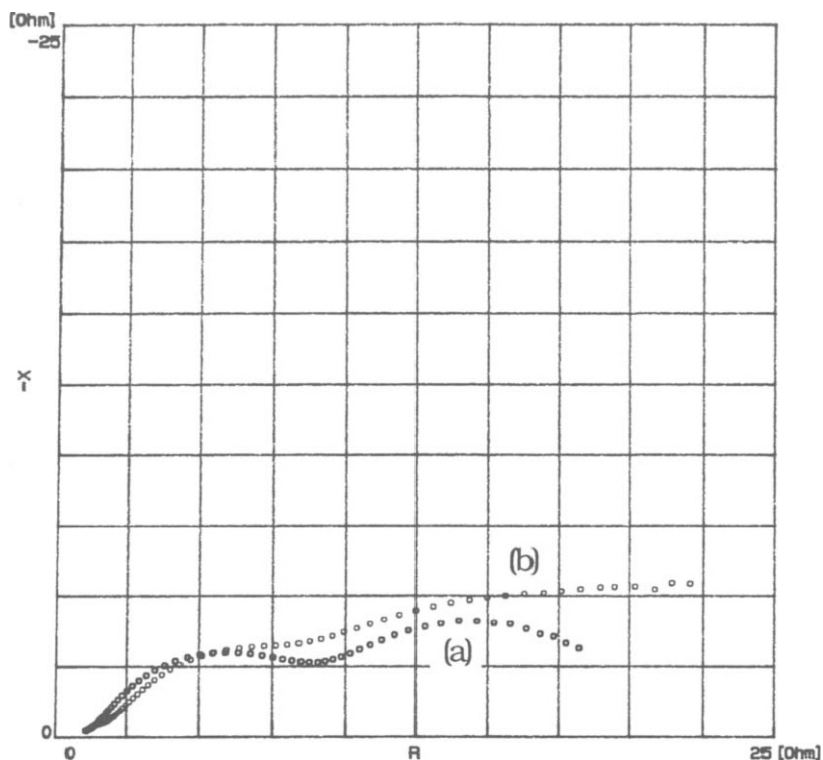


Fig. 6. Cole-Cole plot of Li/a- V_2O_5 cells: (a) cycled between 1.8 and 3.3 V, and (b) cycled between 1.8 and 3.5 V.

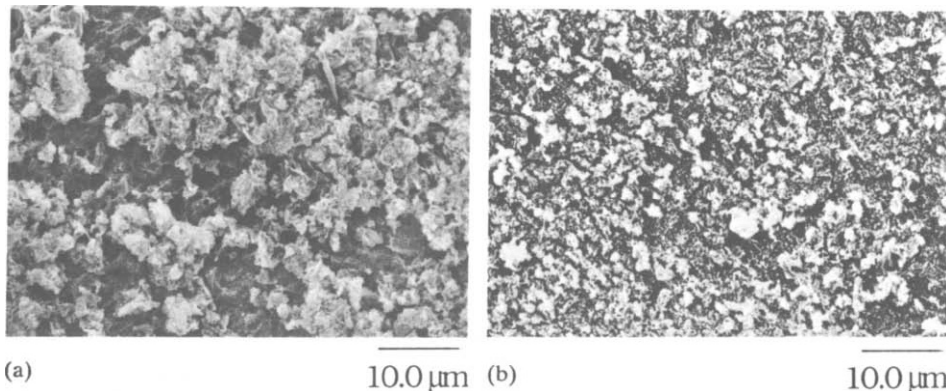


Fig. 7. SEM images of lithium anodes after 4th discharge: (a) cycled between 1.8 and 3.3 V, and (b) cycled between 1.8 and 3.5 V.

The SEM images in Fig. 7 show that vanadium deposition increases the roughness of the Li anode. Generally, an increase in anode roughness results in a decrease in thermal stability, as assumed by Wilkinson *et al.* [2]. Therefore, the stability improvement

of vanadium-deposited Li anodes may mainly depend on the features of the passivation film, rather than on surface anode morphology.

Conclusion

The thermal stability of a-V₂O₅/Li cells was investigated. Vanadium compounds dissolved from the cathode during charge/discharge cycles and were deposited on the anode. It was determined that vanadium-deposited Li has less reactivity. Chemical-state analysis and a morphological investigation of the Li anodes suggested that the improvement in stability was primarily due to the passivation film.

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