# ELECTROCHEMICAL BEHAVIOUR OF AMORPHOUS $V_2O_5(-P_2O_5)$ CATHODES FOR LITHIUM SECONDARY BATTERIES

Y. SAKURAI, S. OKADA, J. YAMAKI and T. OKADA*

*NTT Electrical Communications Laboratories, NTT, Tokai, Ibaraki-ken, 319-11 (Japan)*

## Summary

The electrochemical behaviour of amorphous vanadium oxides (a-$V_2O_5$ and a-$V_2O_5$-$P_2O_5$) cathodes in lithium cells has been investigated. The reversibility of the cathodes is superior to that of c-$V_2O_5$ and the cathodes can operate for >300 cycles. The relationship between cathode composition and cycle performance has been determined, and $P_2O_5$, as a network-former, has been found not to harm the reversibility of cathodes. The degradation in capacity with cycling of the Li/a-$V_2O_5$(-$P_2O_5$) system is due to deterioration of the anode, *i.e.*, an increased polarization on discharge.

## Introduction

Many cathode active materials (CAMs), which can incorporate $Li^+$ ions reversibly, have been widely investigated [1]. Specifically, crystalline CAMs, such as $NbSe_3$, $TiS_2$, $V_6O_{13}$, etc., have been examined from a crystallographic point of view. In recent years, amorphous materials have attracted attention because of their unique isotropic, flexible and low-density structure. The Exxon group has extensively studied amorphous transition metal chalcogenide CAMs, and has reported [2] the superior electrochemical properties of a-$MoS_3$. However, the performance of the latter compound is still below that required for the practical application of lithium cells. Other investigators have also evaluated a-CAMs as reversible cathodes, *e.g.*, a-$LiV_3O_8$ [3] and a-$Cr_3O_8$ [4]. In 1984, the authors demonstrated [5] the rechargeability of amorphous $V_2O_5$-$P_2O_5$ CAM; these studies reversed the previous understanding that a-$V_2O_5$-$P_2O_5$ ($V_2O_5$ 60 mole%) could not be recharged [6]. This paper reports detailed studies of the electrochemical behaviour of a-$V_2O_5$-$P_2O_5$, especially in comparison with that of c-$V_2O_5$.

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*Present address: Research and Development Division, Hitachi Chemical Co. Ltd., Shimodate, Ibaraki-ken, 308, Japan.

## Experimental

a-V$_2$O$_5$–P$_2$O$_5$ (95 - 60 mole% V$_2$O$_5$) compounds were prepared by melting reagent-grade raw oxides in platinum crucibles for 1 h at 750 °C, followed by quenching on a water-cooled iron block. Pure a-V$_2$O$_5$ was obtained by the single-roll quenching technique. X-ray diffraction (XRD) studies and thermal analysis indicated that these vitreous oxides were amorphous. The cathode preparation, cell assembly, and electrochemical techniques used in the studies have been described previously [5]. The "apparent" chemical diffusion coefficients of Li$^+$, $\widetilde{D}$, were measured by a galvanostatic pulse relaxation technique [7], using discs of the Teflon-bonded cathode mixture. The electrolytes were 1 M LiClO$_4$ in a 1:1 (by volume) mixture of propylene carbonate (PC) and dimethoxyethane (DME), and 1.5 M LiAsF$_6$ in 2-methyltetrahydrofuran (2-MeThF). Unless otherwise noted, the latter electrolyte was used.

## Results and discussion

Cells using a-V$_2$O$_5$–P$_2$O$_5$ CAMs were cycled between 2 V and 3.5 V at 0.5 mA cm$^{-2}$. The cell discharge profiles and characteristics at the 100th cycle are given in Fig. 1 and Table 1, respectively. The cycling profile at a low rate
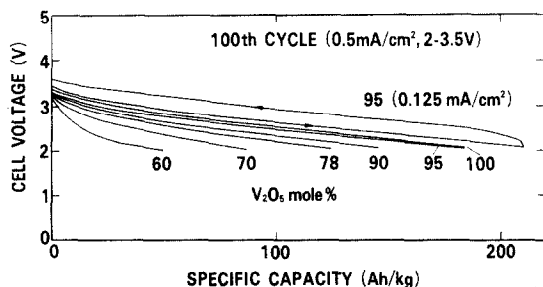


Fig. 1. Discharge profiles of a-V$_2$O$_5$–P$_2$O$_5$ CAMs at 100th cycle.

TABLE 1

Cathode characteristics of a-V$_2$O$_5$–P$_2$O$_5$ CAMs at 100th cycle (0.5 mA cm$^{-2}$, 2 - 3.5 V)

| V$_2$O$_5$ content (mole%) | Residual Li (Li/mole) | Reversible Li uptake | |
|---|---|---|---|
| | | (Li/mole) | (Li/V) |
| 100 | 0.53 | 1.29 | 0.65 |
| 95 | 0.66 | 1.23 | 0.65 |
| | 0.55* | 1.42* | 0.75* |
| 90 | 0.78 | 1.00 | 0.56 |
| 78 | 0.85 | 0.81 | 0.52 |
| 70 | 0.74 | 0.56 | 0.40 |
| 60 | 0.71 | 0.32 | 0.27 |

*0.125 mA cm$^{-2}$.

for a CAM of a-95 mole% $V_2O_5$–$P_2O_5$ is also shown in Fig. 1. Not one of the CAMs exhibited the voltage plateau usually found with a two-phase reaction. It is therefore concluded that $P_2O_5$ acts as a network-former, and that V is only effective in the $Li^+$ accommodation reaction through its valence change. The reversible uptake of lithium (*i.e.*, Li/V ratio) of a-CAMs ($V_2O_5 \gtrsim 80$ mole%) is similar to that of $V_6O_{13}$ (Li/V = 0.5 - 0.6) [8]. With a-CAMs ($V_2O_5 \gtrsim 80$ mole%), some of the inserted $Li^+$ ions were trapped in the host structure within a few cycles and could not be recharged. Although attempts were made to raise the end-of-charge voltage (*i.e.*, 3.5 V → 4.0 V), and thereby to widen the cycling voltage region, by using a PC/DME//1 M $LiClO_4$ electrolyte, which has a higher oxidation potential and conductivity than 2-MeTHF/1.5 M $LiAsF_6$, only a slight gain (~20%) in charge efficiency was observed at 0.5 mA $cm^{-2}$. The amount of residual lithium closely corresponded to the low-diffusion coefficient region (see Fig. 2) for a-95 mole% $V_2O_5$–$P_2O_5$.

The data given in Fig. 3 demonstrate the superior reversibility of amorphous $V_2O_5$–$P_2O_5$ compared with crystalline $V_2O_5$. While the capacity of c-$V_2O_5$ gradually degraded with cycling, that of a-$V_2O_5$–$P_2O_5$ remained virtually constant. These findings clearly confirm previous proposals of the authors [5]. The slight losses in the capacity of a-CAMs observed after the
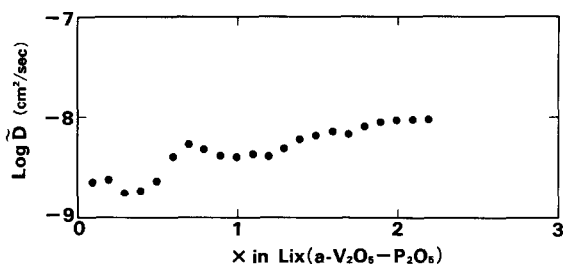


Fig. 2. Relation between apparent chemical diffusion coefficient of a-95 mole% $V_2O_5$–$P_2O_5$ and amount of $Li^+$ inserted.
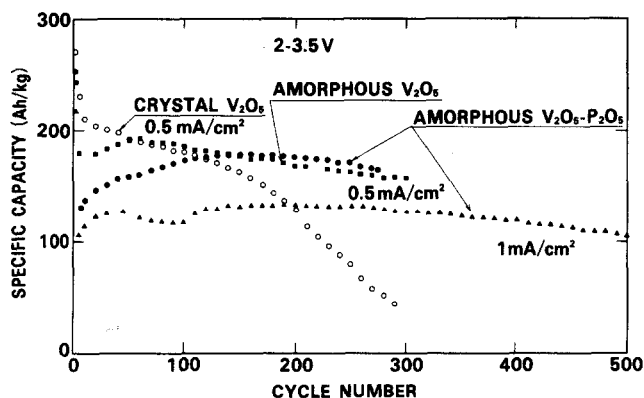


Fig. 3. Capacity change with cycling. (Li/c-$V_2O_5$, Li/a-$V_2O_5$ and Li/a-$V_2O_5$–$P_2O_5$).
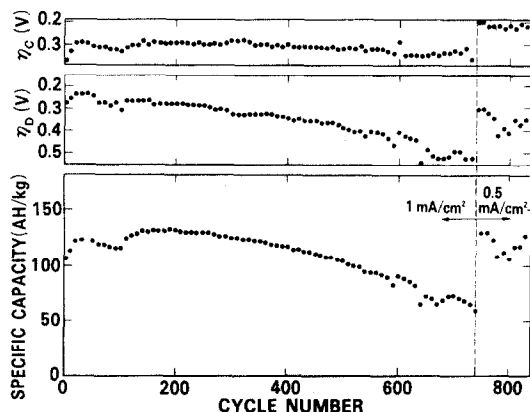
Fig. 4. Relationship between capacity and overvoltage measured at the end of discharge and charge.

200th cycle were due to an increase in the lithium electrode polarization (see below).

Figure 4 shows the relationship between cycling capacity and the change in overvoltage ($\eta$) with cycling. A decline in the capacity coincides with a change in the discharge overvoltage ($\eta_D$) and is apparently independent of the charge process. Studies have indicated [9] that prolonged cycling of lithium electrodes results in an increase in the discharge overvoltage due to the formation of an inactive film on the electrode. Although $\eta_D$ and $\eta_C$ in Fig. 4 also include contributions from the ohmic drop and cathode overvoltage, the changes in $\eta_D$ and $\eta_C$ during cycling are in good agreement with results from cycling tests of lithium electrodes. Therefore, it is concluded that the decline in capacity of the Li/a-$V_2O_5$-$P_2O_5$ cell is due to failure of the lithium electrode.

The relationship between $V_2O_5$ content in a-$V_2O_5$-$P_2O_5$ and cycle performance is presented in Fig. 5. Although the capacities of the a-CAMs decreased with decrease in the $V_2O_5$ content, as was expected, the overall inherent rechargeability clearly demonstrated the stability of a-$V_2O_5$-$P_2O_5$ CAM electrodes in extended cycling. It is clear that $P_2O_5$, as a network-former, does not harm the reversibility of a-CAMs. It should be noted that the phenomenon of decreasing capacity, particularly found in $V_2O_5$-rich a-CAMs, is not due to cathode degradation, but rather is caused by anode
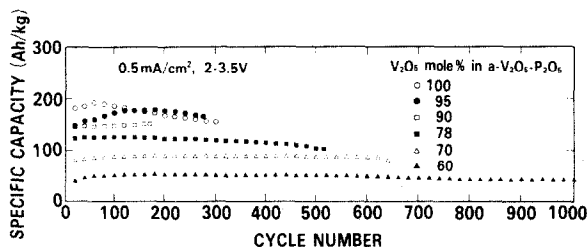


Fig. 5. Dependence of capacity on composition of a-$V_2O_5$-$P_2O_5$.

deterioration. In fact, replacement of the anode with a fresh lithium electrode after test termination resulted in a recovery of the initial capacity and further cycling performance. Clearly, rechargeable $Li/a$-$V_2O_5$-$P_2O_5$ cells with improved high energy density and service life will be achieved if a means can be found to suppress deterioration of the anode during charge/discharge cycling.

## Acknowledgements

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