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A solid state lithium concentration cell with $Li_xV_2O_5$

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A solid state lithium concentration cell $Li_xV_2O_5$/LISICON/$Li_{0.25}V_2O_5$ ($0.25 \leqslant x \leqslant 0.55$) was investigated. The open circuit voltage increased monotonously from about 0 mV at $x = 0.25$ to about 270 mV at $x = 0.55$. Cells with various x-values in the single phase showed similar polarization curves, and their cathode polarizations were slightly larger than the anode polarizations. The cathode potential vs a platinum wire as the third electrode was nearly constant under nitrogen flow, but the anode potential decreased with increase of the lithium content of the sample. During the experiment, Lisicon was satisfactorily stable in contact with $Li_xV_2O_5$.

1. Introduction

Rechargeable lithium cells have attracted attention in view of their high voltage and high energy density. Studies on such secondary cells have mainly been made for organic solvent–lithium salt systems [1], whereas studies on reversible cells with solid Li^+ ion conductor are very few. For example, Lisicon ($Li_{14}ZnGe_4O_{16}$) is well known to be an excellent Li^+ ion conductor [2], but its application to a solid state lithium cell has not been demonstrated. However, there is a need to develop appropriate active electrode materials for such a solid electrolyte cell. Li^+ ion-electron mixed conductors such as ternary bronze type oxides [3] are suitable electrode materials for such cells.

Lithium vanadium oxides, $Li_xV_2O_5$, exist as a series of non-stoichiometric phases [4–8]: α, β and γ. Among the phases, the β phase has the widest homogeneous range [9] and shows ionic and electronic mixed conduction [10], which is an important property for a cathode material. The present authors reported the preparation procedure of $Li_xV_2O_5$ and the homogeneous range of the β phase in a previous paper [9]. A cell Li/solid electrolyte/$Li_xV_2O_5$ would be expected to give a high voltage and high energy density. Prior to the investigation of such a cell, a lithium concentration cell was composed from the solid electrolyte Lisicon and the oxide bronze $Li_xV_2O_5$ [11]. In this paper, the fundamental characteristics, such as the open circuit voltages (OCVs), polarization phenomena and constant current discharges, will be described mainly as a function of the lithium content x in $Li_xV_2O_5$.

2. Experimental details

The samples of $Li_xV_2O_5$ were prepared by solid state reaction of $LiVO_3$, V_2O_5 and V_2O_3. The prescribed amounts of powder were weighed, mixed in a ball-mill using acetone as a dispersing agent, and dried under an IR lamp. The powder was pressed into tablets (13 mm diameter and 3 mm thick) under 200 MPa pressure and the tablets were heated in a platinum boat at 560° C for 18 h under a nitrogen gas flow (about 120 ml min^{-1}). The samples thus obtained were ground sufficiently and pressed again isotropically into tablets (10 mm diameter and 3 mm thick) under 300 MPa pressure. The tablets were heated again at 560° C for 11 h under a nitrogen flow. The nitrogen gas used here was first passed through a double column filled with activated copper–diatomaceous earth particles, and then through a molecular sieve column, a silica gel column, and a double tube packed with phosphorous pentoxide, in sequence. The gas thus treated was regarded as sufficiently purified.

Lisicon was prepared from GeO_2, ZnO and

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Li_2CO_3 [2]. The mixed powder of the starting chemicals was pressed into tablets and heated at 1050° C for 11 h in air. The tablets were ground and pressed again isotropically under 300 MPa pressure into tablets (10 mm diameter and 3 mm thick) which were buried in a powder of the same composition and sintered at 1050° C for 2 h in air.

The solid state lithium concentration cell was composed of a Lisicon tablet and two lithium vanadium oxide tablets [10]. The composition of the cathode tablet was fixed at $Li_{0.25}V_2O_5$ since it was fairly stable and had a composition near the lower limit of the β phase. Therefore, the cell can be written as follows:

$$Pt/Li_xV_2O_5/Lisicon/Li_{0.25}V_2O_5/Pt \quad (1)$$

The lithium content, x, ranged from 0.15 to 0.70, although the samples of $0.15 \leqslant x \leqslant 0.22$ and $0.55 \leqslant x \leqslant 0.70$ were the mixed phases of α and β, and β and γ, respectively [9].

The cell was set in a stainless-steel vessel and purified nitrogen gas was introduced into it to avoid reactions of $Li_xV_2O_5$ with air. After the cell was heated at 450° C for about 30 min in order to promote the contact between each tablet, the cell properties were examined in the temperature range 200–400° C. After the first discharge was terminated, the cell was charged by the quantity of electricity utilized during the discharge. The second discharge was conducted in the same manner as the first discharge, and so on. Constant current discharges were also carried out in a similar manner to that mentioned above. When the anode and cathode polarizations were examined, a platinum wire (0.05 mm diameter) was wound on the side face on the Lisicon tablet.

3. Results and discussion

The OCVs of the cell (1) are shown in Fig. 1. The values were obtained when the OCV change became within ± 1.0 mV during 1 h at a given temperature. When the lithium content x in the anode was the same as that of the cathode, the OCVs were zero within experimental error, as seen in Fig. 1a. The cells with anodes of x lower than 0.20 showed almost the same curves as Fig. 1a except for the slightly lower values. On the other hand, the cells with x higher than 0.55 gave curves analogous to Fig. 1e. It is noticeable that the OCVs increased linearly with increasing temperature. Assuming that the enthalpy change can be neglected in the solid state cell reaction in the temperature region of this work, the slopes of the curves designate the entropy changes ($nF \cdot OCV = -\Delta G \risingdotseq \text{constant} + T\Delta S$). The slope increasing with x in Fig. 1 revealed that the entropy change in the cell increased with an increase of the difference of lithium content between the anode and the cathode. The entropy change seemed to be caused predominantly by the change of the lithium configuration in the anode because the state of the cathode was fixed or independent of the anode composition. According to Wadsley [12], the β phase of $Li_xV_2O_5$ can contain crystallographically the maximum packing of lithium at the composition $Li_{0.66}V_2O_5$, so the packing rate decreases with decreasing x. The slopes in Fig. 1 suggest that the change in the degree of lithium packing influence the entropy change in the higher region of x more than in the lower region of x.

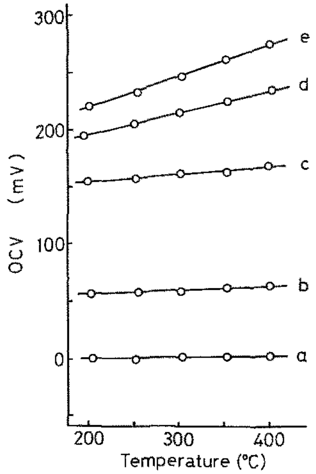

Fig. 1. OCVs of the cell $Li_xV_2O_5/Lisicon/Li_{0.25}V_2O_5$. x in the anode was (a) 0.25, (b) 0.30, (c) 0.40, (d) 0.50 and (e) 0.55.

Fig. 2 shows the polarization curves of the cell with the anode of $x = 0.30$ in relation to the number of charge–discharge cycles. The first polarization curve falls lower than the other curves. This seemed to be due to the fact that the initial contact between the electrolyte and the electrode was inadequate. Through the first discharge and the successive charge, the contact

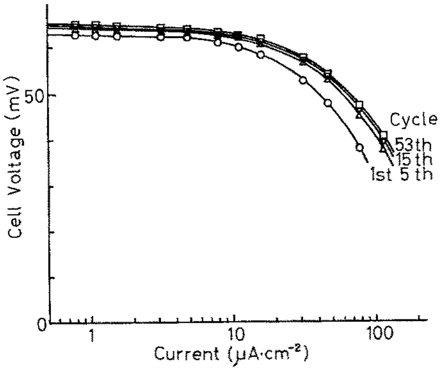

Fig. 2. Polarization curves of a cell $Li_{0.30}V_2O_5$/Lisicon/$Li_{0.25}V_2O_5$ at 400° C after different number of charge–discharge cycles.

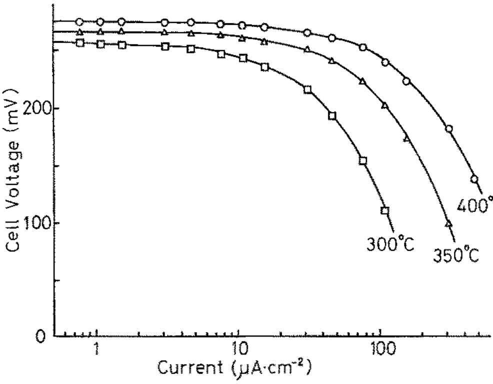

Fig. 4. Temperature-dependence of polarization characteristics of a cell $Li_{0.55}V_2O_5$/Lisicon/$Li_{0.25}V_2O_5$.

among the tablets improved and Li^+ ion would be able to migrate more easily after the first discharge. The capacity of the cell was maintained through many discharge–charge cycles, as shown in Fig. 2.

The polarization curves like those shown in Fig. 2 could be obtained also for the other cells with x larger than 0.30. Fig. 3 indicates several polarization characteristics obtained from the steady-state curves for the individual cells. The cell voltage increased with increasing lithium content in the anode, and it reached a maximum voltage for the cell with $x = 0.55$, although the anode of $x = 0.55$ contained a trace amount of the γ phase as well as the β phase. On the other hand, the polarization characteristics of cells utilizing the anode in the β single phase region were almost identical to and independent of the anode composition, but the cells with the anode of the mixed phase showed slightly larger polarization than those with the single phase anode.

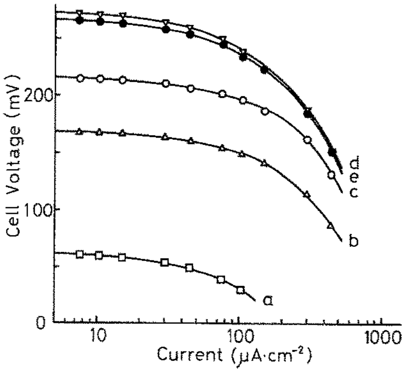

Fig. 3. Polarization characteristics of cells $Li_xV_2O_5$/Lisicon/$Li_{0.25}V_2O_5$ at 400° C where x was (a) 0.30, (b) 0.40, (c) 0.50, (d) 0.55 and (e) 0.60.

The change in the polarization of the cell which gave the highest cell voltage in Fig. 3 is shown as a function of the measuring temperature in Fig. 4. The cell voltages at low current density did not differ appreciably from each other, but the polarization at higher current density increased with lowering of temperature. Considering the dependence of the electrical conductivities of both Lisicon and the lithium vanadium bronze on temperature [9], the main overpotential would be the resistance overpotential.

Fig. 5 shows the result of the constant current discharge with a cell $Li_{0.50}V_2O_5$/Lisicon/$Li_{0.25}V_2O_5$. The discharge at 7.3 μA cm^{-2} was followed by a charge with the same quantity of electricity, and after the charge, the second discharge at 36 μA cm^{-2} was started at the same temperature, and so on. The energy densities were estimated for the cut-off voltage of 150 mV:

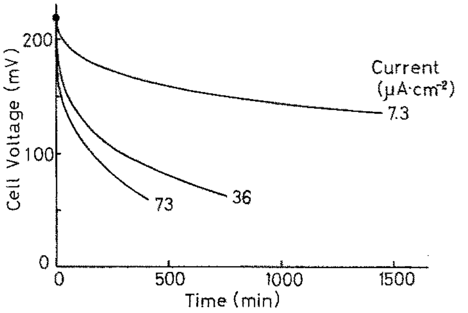

Fig. 5. Constant current discharge curves of a cell $Li_{0.50}V_2O_5$/Lisicon/$Li_{0.25}V_2O_5$ at 400° C.

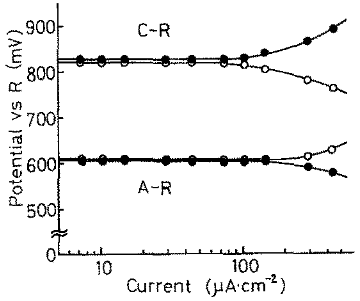

Fig. 6. Cathode and anode potential curves of a cell $Li_{0.50}V_2O_5$/Lisicon/$Li_{0.25}V_2O_5$. Open and solid circles designate discharge and charge characteristics, respectively.

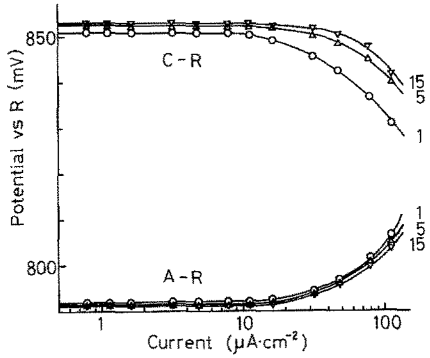

Fig. 7. Polarization curves of a cell $Li_{0.30}V_2O_5$/Lisicon/$Li_{0.25}V_2O_5$ at 400° C. C–R and A–R indicate the cathode and anode potential vs platinum reference electrode, respectively and the numbers give the number of discharge cycles.

they were 2.4, 3.0 and 9.1 mWh kg^{-1} in order of the current.

The anode and cathode polarizations were measured individually in order to examine which polarization was predominant. In this experiment, a platinum wire was attached on the side face of the electrolyte tablet as a third electrode. Fig. 6 shows one of the results which were obtained with current supplied positively and negatively. The potentials and the form of the curves shown in this figure changed little even after many tens of cycles. But, when the flow rate of the surrounding gas or the gas itself was changed, the potentials varied slightly and then settled to new values in a comparatively short time. The potentials appeared, therefore, to be influenced by change in the partial pressure of oxygen contained in the flowing gas.

The function of the platinum wire working as a third electrode could not be analysed in this study, but the following mechanism is suggested on the basis of the results mentioned above.

(a) 1st step: a trace amount of Li_2O in Lisicon contacing the platinum electrode offers lithium according to the following reactions

$$Li_2O \rightleftharpoons 2Li + 1/2O_2 \qquad (2)$$

$$Li \rightleftharpoons Li^+ + e \qquad (3)$$

(b) 2nd step: lithium interacts with platinum to produce an alloy Pt(Li) [13]

(c) 3rd step: lithium in Pt(Li) equilibrates to Li^+ ion in the solid electrolyte under given partial pressure of oxygen

According to the mechanism proposed here, the potential of the third electrode would be maintained in steady-state so long as the partial pressure of oxygen was kept constant. Thus, the platinum wire could be considered to work as a reference electrode in this experiment.

Fig. 7 indicates the anode and cathode polarization curves of a cell corresponding to that quoted in Fig. 2. Compared with the anode polarization, the cathode polarization varied a little after the repetition of discharge, and the overpotential of the cathode was somehwat larger than that of the anode. The variation of the cathode polarization after successive discharge could be due to the difference in the state of contact of the tablets before and after the repetition of discharge. The features shown in Fig. 2 analogous to these curves could be ascribed mainly to the cathode polarization.

Fig. 8 shows the polarization curves of several

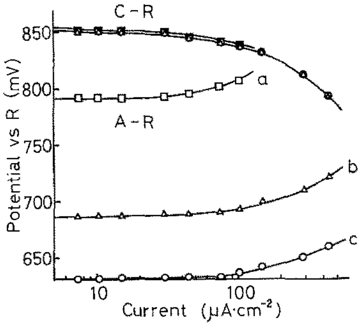

Fig. 8. Cathode and anode potential curves in the cells $Li_xV_2O_5$/Lisicon/$Li_{0.25}V_2O_5$ where x was (a) 0.30, (b) 0.40 and (c) 0.50.

cells. As expected, all the cathode polarization curves were identical regardless of the anode composition. In other words, the cathode potential vs the reference electrode showed reproducible steady-state values. On the other hand, the potential curve of the anode dropped gradually with increasing lithium content of the anode. The drop of the anode potential vs the reference electrode was related to the increasing total conductivity of the sample with increase of x [9]. The increase of the Li^+ ion content in the vanadium oxide bronze caused the increase of the concentration of V^{4+} ion to hold the electric neutrality condition, and in turn the increase of the concentration of the hopping electron [14] produced by the reaction

$$V^{4+} \rightleftharpoons V^{5+} + e \qquad (4)$$

These experimental results suggest that the potential of any electrode vs the third electrode was determined by the ability of the electrode material to produce conductive electrons. Therefore, the potential in this work seemed to be controlled by the V^{4+} ion content of the sample.

4. Summary

A solid state lithium concentration cell was studied by using lithium vanadium oxide bronze $Li_xV_2O_5$ and a solid electrolyte Lisicon. The OCVs of the cell $Li_xV_2O_5$/Lisicon/$Li_{0.25}V_2O_5$ increased with the lithium content x in the β single phase region. The cathode polarization was shown to be larger than the anode polarization by use of a platinum wire as a third electrode. The anode potential vs the third electrode decreased with x, while the cathode potential remained constant.

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