

Electrochemical characteristics of calcium in organic electrolyte solutions and vanadium oxides as calcium hosts

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Abstract

We investigated batteries using calcium as the transfer ion with a view to developing high energy density and safe ion-transfer type batteries as an alternative to lithium-ion batteries. The electrochemical behavior of calcium electrodes in various kinds of electrolyte solution was investigated by means of galvanostatic measurements. The anodic dissolution proceeded easily, but there was no cathodic deposition in the solutions we tested in this study. As a result, we used $\text{Ca}(\text{ClO}_4)_2$ solute/acetonitrile solution to evaluate the calcium insertion behavior. Moreover, we examined electrochemical insertion and extraction reactions with respect to calcium ions using vanadium oxides as calcium host materials. Their discharge curves indicated that a calcium insertion reaction did indeed occur. Structural changes in vanadium oxides resulting from the insertion and extraction of calcium ions were observed for the first time.

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1. Introduction

Recently attention has focused on ion-transfer type batteries that use polyvalent cations such as Mg^{2+} [1–5], Ca^{2+} [5,6], Zn^{2+} [7], Al^{3+} [7] and Y^{3+} [5]. This is because of the natural abundance, chemical safety and low cost of these metals in comparison with lithium. Moreover, the use of polyvalent cations is the key to obtaining much larger discharge capacities than those of lithium-ion batteries. The cell performance of these batteries is affected by such cation characteristics as the ionic radius and the standard electrode potential (SEP). There have been a number of studies on batteries with Mg ions as the transfer ions. This is because of the ionic radius of a magnesium ion similar to that of a lithium-ion. For example, Aurbach et al. reported that rechargeable magnesium batteries using a system consisting of $\text{Mo}_3\text{S}_4/0.25 \text{ mol dm}^{-3} \text{ Mg}(\text{AlCl}_2\text{BuEt})_2$ in THF (Bu: butyl, Et: ethyl, THF: tetrahydrofuran)/Mg had an open-circuit voltage of 2.0 V, a first discharge capacity of 75 mAh g^{-1} , and a cycle life of about 600 cycles [4]. They revealed that magnesium ions were intercalated into the sulfide materials and the system worked as a rechargeable battery. However, batteries employing magnesium ions

exhibit only low voltages because their anode SEP (-2.36 V versus NHE) is more positive than that of lithium (-3.05 V). By contrast, calcium has rarely been investigated as the transfer ion because of its large ionic radius [5,6] but its SEP (-2.87 V) is comparable to that of lithium making it very attractive in terms of the fabrication of high-voltage/energy density batteries. Considering these circumstances, we selected calcium ions in order to obtain high-voltage batteries, and we investigated the electrochemical characteristics of calcium electrodes in several kinds of electrolyte solution.

Calcium host materials require sufficient crystallographic space in which to insert the calcium ions because the ionic radius of calcium is larger than that of lithium. So far various kinds of electrode material have been investigated as the lithium host. Amatucci et al. reported that nanocrystalline vanadium oxides were available as host materials for the insertion and extraction of Mg^{2+} , Ca^{2+} and Y^{3+} . They studied trivalent yttrium in particular in order to obtain higher discharge capacities, and revealed that the yttrium ions could be reversibly intercalated into the host material accompanying the crystal structural changes [5]. In this study, we intensively investigated the insertion and extraction behavior of the calcium ions using crystalline vanadium oxides and amorphous vanadium oxides, which were reported by Sakurai et al. [8] to enhance lithium-ion insertion due to their amorphous structure. Moreover, the struc-

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tural changes in vanadium oxides were investigated after the discharge and charge tests.

2. Experimental

We examined several kinds of electrolyte solution including propylene carbonate (PC), dimethylcarbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), γ -butyrolactone (GBL), *N,N*-dimethylformamide (DMF) and acetonitrile (AN) as solvents to evaluate the electrochemical behavior of the calcium electrodes. An amount of 1 mol dm^{-3} $\text{Ca}(\text{ClO}_4)_2$ was used as the solute in these solvents. All electrolyte solutions were purchased from Kishida Chemicals Co. Ltd. Electrochemical measurements were carried out using a beaker-type three-electrode system. Calcium sheet electrodes (Furuuchi Chemical Co. Ltd., 0.5 mm thick, 1 cm^2) were used as the working and counter electrodes. Both electrodes were prepared by cold-pressing a calcium sheet on a Ti mesh. The working electrode potential transients were measured under the galvanostatic condition of $50 \mu\text{A cm}^{-2}$ for 1 h in both the oxidation and reduction processes. The overpotential with respect to the oxidation and reduction reaction was investigated by using a symmetrical electrochemical cell including two calcium electrodes with the same shape. The electrode potential was monitored using silver wire, separated from the electrolyte by frit glass, immersed in the same solvent as the electrolyte containing 0.1 mol dm^{-3} AgNO_3 and 0.01 mol dm^{-3} tetrabutyl ammonium perchlorate as the reference electrode. Changes in the electrode weight were measured before and after the electrochemical reactions to confirm whether or not these reactions could indeed occur.

Vanadium oxides, which are well known as lithium hosts, were evaluated as calcium host materials. Three kinds of vanadium oxide, crystalline V_2O_5 (c- V_2O_5), amorphous V_2O_5 (a- V_2O_5) and amorphous $(\text{V}_2\text{O}_5)_{0.95}(\text{P}_2\text{O}_5)_{0.05}$ (a-

V_2O_5 - P_2O_5 , with P_2O_5 as a crystallization inhibitor), were prepared as reported elsewhere [8]. The substitution of a small quantity of P_2O_5 for V_2O_5 prevented crystallization and thereby produced an amorphous oxide. The amorphous states of a- V_2O_5 and a- V_2O_5 - P_2O_5 were confirmed by X-ray diffraction (XRD) analysis (Rigaku Co. Ltd., RINT2500HF) with Cu $K\alpha$ radiation. Working electrodes including these oxides were prepared by the following procedure. The oxide powder was mixed with acetylene black and PTFE with a weight ratio of 70:25:5. The mixture was then rolled into a 0.6 mm thick sheet and cut into pellets 6 mm in diameter. The pellets were then pressed on a Ti mesh. In our evaluation of the host materials, the other cell components were the same as those used for the above-mentioned measurements. The structural changes in the vanadium oxides that accompanied the ion insertion and extraction were investigated by using XRD analysis.

All experiments were carried out in dry air at room temperature.

3. Results and discussion

Fig. 1 shows the dependence of the electrode potential of calcium (working electrode) in several kinds of electrolyte solution. In the oxidation process, the electrode potential was rather positive in ester carbonate-based solutions such as PC and EMC, but the potential was rather stable in AN- and DMF-based solutions. In the reduction process, the overpotential of the calcium electrodes increased rapidly in almost of all the solutions, the calcium electrode exhibited a comparatively small overpotential and stable behavior only in the AN-based solution. Among these tested solutions, only the AN-based solution exhibited a small overpotential and stable behavior in both processes.

On the basis of the above results, we focused on the AN-based solution and measured the weight of the calcium

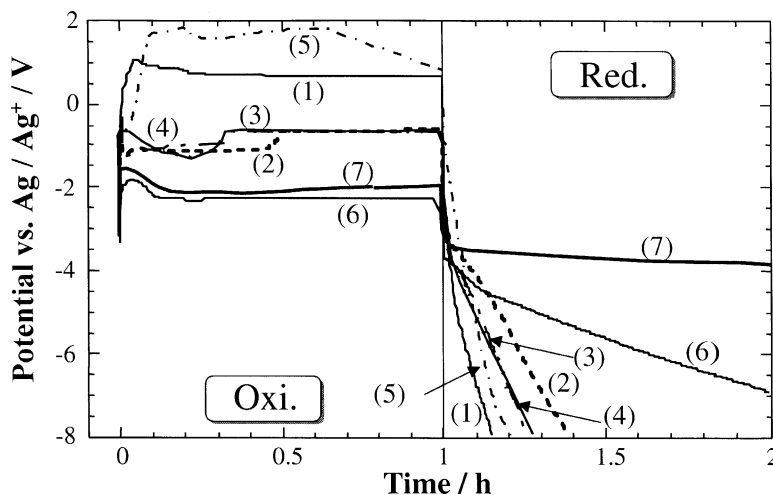


Fig. 1. Dependence of calcium electrode potential on time under a galvanostatic condition of $50 \mu\text{A cm}^{-2}$ in an electrolyte solution of 1 mol dm^{-3} $\text{Ca}(\text{ClO}_4)_2$ /solvent. Solvent: (1) PC; (2) DMC; (3) DEC; (4) EMC; (5) GBL; (6) DMF; and (7) AN.

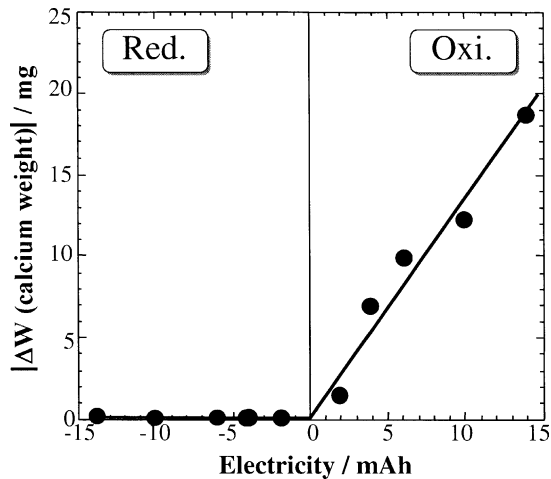


Fig. 2. Weight changes of calcium electrodes upon electrochemical reduction and oxidation treatment.

electrodes to confirm the electrochemical dissolution and deposition reaction. Fig. 2 shows the dependence of the calcium weight changes on the quantity of electricity passed between the working and counter electrodes in the AN-based solutions. As shown in this figure, there was a decrease in the calcium weight that was almost linearly proportional to the quantity of electricity used in the oxidation process. In contrast, there was no weight increase as a result of the reduction process. These results suggest that calcium dissolved easily in the solution during oxidation but that there was no calcium deposition during reduction. During the reduction process, solvent (or solute) decomposition

appeared to be taking place on the electrode. Such electrode behavior is unfavorable if it is used as the counter electrode in evaluating the host materials to develop the calcium-ion batteries. However, as shown in Fig. 1, AN-based solutions were found to exhibit comparatively small overpotential for the calcium dissolution. This behavior enables the calcium electrode to work as the counter electrode in the AN-based solutions when evaluating the host materials in terms of calcium insertion behavior as described later.

We examined the electrochemical characteristics of vanadium oxides when used as positive electrodes with calcium as the negative electrodes. Fig. 3 shows discharge curves of $c\text{-V}_2\text{O}_5$, $a\text{-V}_2\text{O}_5$ and $a\text{-V}_2\text{O}_5\text{-P}_2\text{O}_5$ in an electrolyte solution of $1 \text{ mol dm}^{-3} \text{ Ca}(\text{ClO}_4)_2/\text{AN}$. We obtained discharge capacities of more than 400 mAh g^{-1} as shown in Fig. 3. The potentials of all electrodes moved rapidly in the negative direction from their open-circuit potential and no distinct plateau regions were observed, which indicated that the diffusion of calcium ions in the oxide lattice was very slow. This behavior is similar with the tendency reported by Amatucci et al. [5]. Amorphous oxides show larger amounts of calcium insertion and smaller overpotential than crystalline oxides. These results imply that the isotropic structure of amorphous oxides enhances calcium-ion insertion [8].

Further investigation using $c\text{-V}_2\text{O}_5$ was carried out to evaluate the structural changes caused by the calcium insertion and extraction. Fig. 4 shows XRD patterns of $c\text{-V}_2\text{O}_5$ untreated, discharged and charged as the calcium hosts. We observed a new phase that accompanied the calcium insertion after discharging as shown in Fig. 4(b). The new phase has some peaks similar to those of the parent phase. These

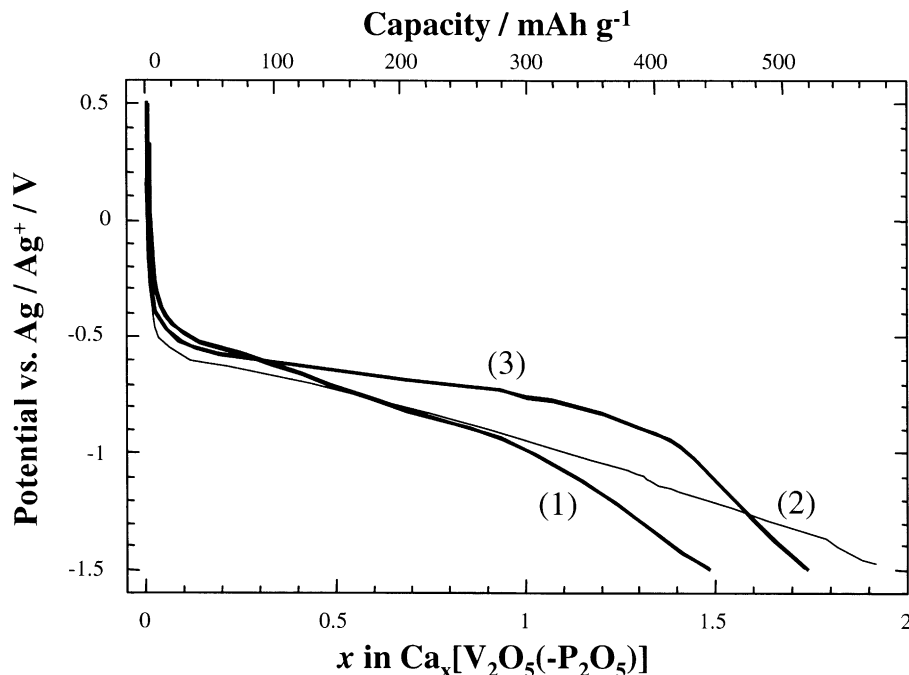


Fig. 3. Discharge curves of vanadium oxides ($c\text{-V}_2\text{O}_5$ (1), $a\text{-V}_2\text{O}_5$ (2) and $a\text{-V}_2\text{O}_5\text{-P}_2\text{O}_5$ (3)) under a galvanostatic condition of $50 \mu\text{A cm}^{-2}$.

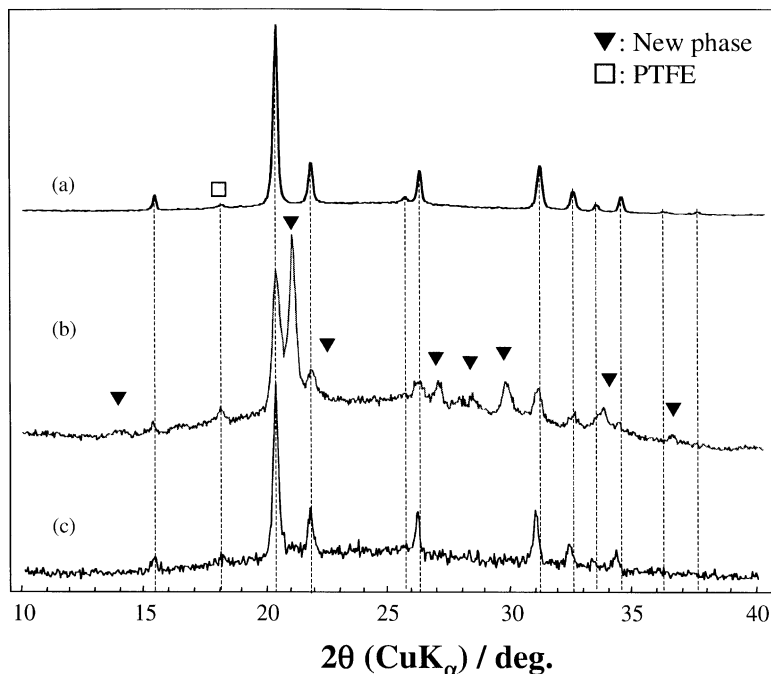


Fig. 4. XRD patterns of $c\text{-V}_2\text{O}_5$ (a) untreated, (b) after discharging and (c) after charging.

peaks corresponded to the formation of a new phase containing calcium ions that resulted from the electrochemical insertion. These results demonstrate that calcium insertion can indeed occur. Moreover, these peaks returned to the parent structure after charging as shown in Fig. 4(c). We will provide a detailed analysis of the results of these structural changes in another paper. As a result, we found that vanadium oxides have structural reversibility on the insertion and extraction of calcium ions. This is the first report on the structural changes caused by calcium insertion and extraction. These results show that vanadium oxides function reversibly as calcium hosts and this makes them promising electrode materials for calcium-ion batteries.

4. Conclusions

We investigated the electrochemical characteristics of calcium electrodes in various kinds of organic electrolyte solutions and vanadium oxides as the calcium hosts. The electrochemical information was obtained by undertaking various electrochemical measurements.

1. Calcium deposition was found not to occur in the solutions tested in this study. By contrast, in the oxidation process, the calcium dissolution was confirmed to proceed easily especially, in AN-based solutions.
2. Batteries using the vanadium oxides as the host materials exhibited discharge capacities of more than

400 mAh g^{-1} . The electrochemical insertion and extraction of calcium ions into and from the vanadium oxides was confirmed by structural changes observed by means of XRD analysis.

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