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SHORT COMMUNICATION

An aqueous rechargeable lithium battery based on LiV_3O_8 and $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$

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1 Introduction

Rechargeable lithium ion batteries with nonaqueous electrolyte solutions have been widely used for powering consumer electronic devices such as cellular phones and laptop computers [1]. However, it is apparently more difficult to make larger lithium ion batteries inherently safe. This is mostly due to the reactivity of the electrode materials with the nonaqueous electrolyte solution constituents. In comparison with cells containing organic electrolyte solutions, rechargeable lithium ion batteries with aqueous electrolyte solutions have many advantages such as low cost of both materials and manufacturing, intrinsic safety and environmental friendliness. This has attracted many researchers [2–12] since its inception [13–15]. This type of battery consists of intercalation compounds for lithium ions as active electrode materials and an aqueous electrolyte solution. Because the stability window of aqueous electrolyte solutions is much smaller than that of non-aqueous solutions, the selection of intercalation materials which de/intercalate lithium ions at a suitable electrode potential is a key factor for the performance of the aqueous battery cell. There are few compounds with flat charge/discharge curves that can be used as positive and negative electrode materials. In addition, the combination of negative and positive electrodes of a rechargeable lithium battery in aqueous electrolytes is of importance in order to obtain good electrochemical performance.

In our earlier work, we reported on the electrochemical performance of an aqueous rechargeable lithium battery (ARLB) using a LiV_3O_8 (negative electrode) and $LiCoO_2$ (positive electrode) in saturated $LiNO_3$ aqueous electrolyte [11], and $LiMn_2O_4$ (positive electrode) in 2 M Li_2SO_4 aqueous solution [16]. These cells exhibit good cycling performance. Here we report on the electrochemical performance of a rechargeable lithium battery using LiV_3O_8 as negative electrode, $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ as positive electrode material, and a 2 M Li_2SO_4 aqueous solution as electrolyte, the results demonstrate the feasibility of this concept.

2 Experimental

Crystalline LiV_3O_8 was prepared by melting a mixture of Li_2CO_3 and V_2O_5 in an appropriate molar ratio at 680 °C and by cooling it slowly down to room temperature [11]. The $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ sample was prepared according to the literature [17]. The crystal structures of all samples were determined by X-ray powder diffraction (XRD) using a Bruker Analytical X-Ray Systems with CuK_α radiation source filtered by a Ni thin plate.

A three-electrode electrochemical cell was employed for cyclic voltammetry (CV) in an unbuffered 2 M Li_2SO_4 solution; its pH was about 7. A saturated calomel electrode (SCE) and Ni-mesh were used as reference and counter electrode, respectively. The preparation of the negative and positive electrodes was conducted in the same way by pressing a powder mixture of the sample, acetylene black and poly(tetrafluoroethylene) (PTFE) in a weight

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ratio of 80:10:10. Galvanostatic charge and discharge measurements of two-electrode glass cell consisting of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ cathode and LiV_3O_8 anode were conducted with a cycler (LAND Electronic Co.) at a constant current density controlled by a personal computer. All electrochemical measurements were performed at ambient temperature.

3 Results and discussion

XRD patterns of the oxides, LiV_3O_8 and $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$,. are shown in Fig. 1. In Fig. 1a, the peak at about $2\theta = 13°$ is assigned to the diffraction by (100) planes indicating the layered structure of LiV_3O_8. These layers consist of VO_6 octahedral and VO_5 trigonal bipyramids which share corners with the octahedral. The observed diffraction lines in Fig. 1b agree well with other XRD patterns [17]. $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ has a rhombohedral structure belonging to the *R3m* space group of a hexagonal α-$NaFeO_2$ structure. The lattice is formed by oxygen atoms in ABC stacking with alternating layers containing mixtures of nickel, cobalt, and manganese atoms.

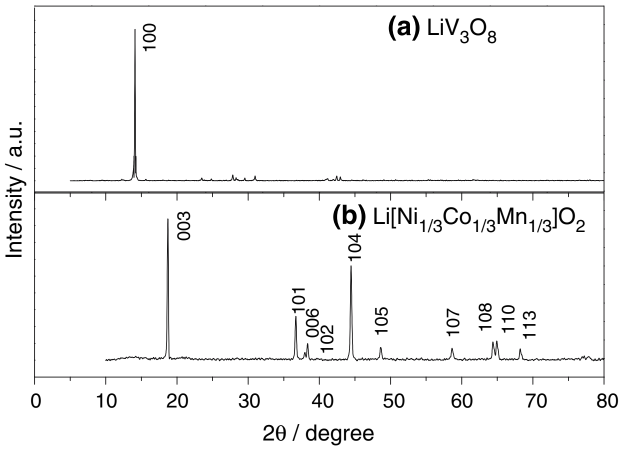


Fig. 1 XRD patterns for (**a**) LiV_3O_8 and (**b**) $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$

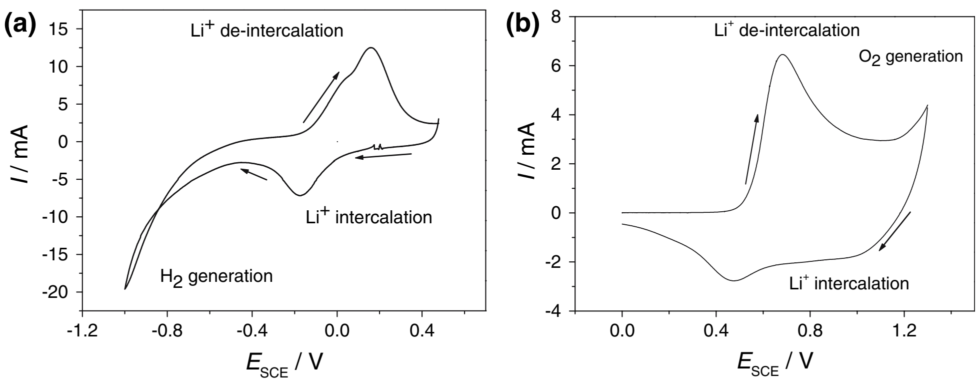
The CV curve (second scan) of LiV_3O_8 in 2 M Li_2SO_4 aqueous electrolyte at a scan rate of 1 mV s^{-1} is shown in Fig. 2a. A pair of peaks corresponding to intercalation and deintercalation of lithium ions can be observed at −0.17 and 0.2 V, respectively. The hydrogen evolution potential shifts to −0.80 V due to the considerable overpotential of the electrode. This shows that LiV_3O_8 can be used as negative electrode material for an ARLB without evident hydrogen evolution.

The second CV scan of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ in 2 M Li_2SO_4 aqueous electrolyte is shown in Fig. 2b. A pair of redox peaks located at 0.48 and 0.68 V corresponds to the intercalation and de-intercalation of lithium ions in $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$, respectively. The oxygen evolution potential shifts up to 1.29 V. This shows that it is possible to extract lithium ions from the host before the evolution of oxygen. $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ can be used as positive electrode material for an ARLB without evident hydrogen evolution at the nickel mesh electrode operating in the oxygen evolution potential range. The above results show that an ARLB can be built using LiV_3O_8 as the negative electrode and Li $[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ as the positive.

The second charge and discharge curves of the LiV_3O_8//$Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ cell in the aqueous electrolyte are shown in Fig. 3. The average discharge voltage of this cell is 0.83 V. It was found that the discharge capacity of the cell was 46.9 mAh g^{-1}, while that for the charge was 67.4 mAh g^{-1}. The coulombic efficiency of the cell was about 69.6%, which is perhaps due to the poor stability of $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ compared with $LiCoO_2$ [1]. However, the lower coulombic efficiency requires further study since other factors such as formation processes may also be effective.

Cycling behavior of LiV_3O_8//$Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ ARLB in the first 10 cycles at 0.2 mA cm^{-2} is shown in Fig. 4. The capacity decreases gradually in the first six cycles and then becomes stable. The capacity of the first cycle is 55.2 mAh g^{-1} and of the tenth cycle is 30.2 mAh g^{-1}. After 10 cycles the capacity remained at only 54.7% of the original capacity. The cycling performance of this ARLB system is

Fig. 2 Cyclic voltammograms (second scans) of (**a**) LiV_3O_8 and (**b**) $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ in 2 M Li_2SO_4 aqueous electrolyte at a scan rate of 1 mV s^{-1}



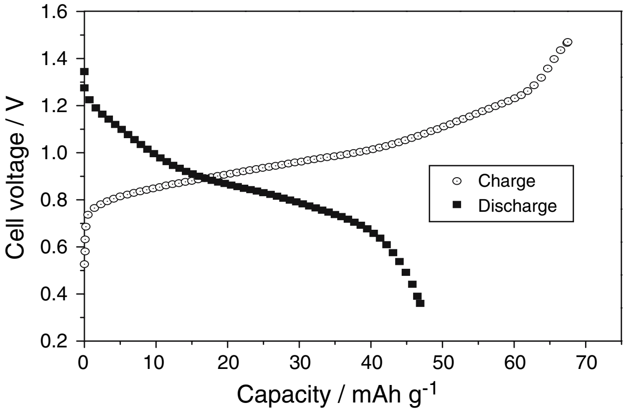


Fig. 3 The second charge and discharge curves of the ARLB cell at 0.2 mA cm^{-2}

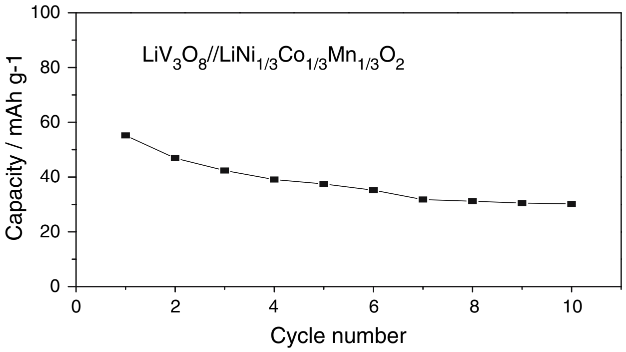


Fig. 4 Cycling behavior of LiV_3O_8//$Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ ARLB in the first 10 cycles at the current density 0.2 mA cm^{-2}

not comparable with our other reported ARLB systems using $LiCoO_2$ or $LiMn_2O_4$ as positive electrodes [11, 16]. The capacity fading mechanism is probably related to the cathode structure since $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ is not stable under storage in air [1] and it was found that the crystallinity decreased after 10 cycles. Further studies of these changes are underway.

4 Conclusion

An ARLB containing LiV_3O_8 as negative electrode, $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ as positive electrode and a 2 M Li_2SO_4 aqueous electrolyte solution has been constructed for the first time based on the good stability of intercalation and deintercalation of lithium ions of LiV_3O_8 and $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$. The average discharge voltage of the ARLB is 0.83 V; the cell can be repeatedly charged and discharged. The capacity is below 50% of the theoretical in organic electrolyte solutions. Initial results suggest that this type of ARLB might be a good candidate as a new energy storage and conversion system. Further research is needed to improve the electrochemical performance such as specific capacity, energy density and cycleability to a level that is comparable with those of the present aqueous rechargeable batteries such as Ni-MH.

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