DOI: 10.1002/anie.200603699

Batteries

An Aqueous Rechargeable Lithium Battery with Good Cycling Performance**

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The development of the world economy and the consequent increase in traffic means that increasing numbers of heavy fuel-powered vehicles are appearing on our roads, resulting in greater pollution of the environment. Electric vehicles (EVs) are a new, developing trend in the world automotive industry, and an important tool for reducing CO_2 emissions and protecting the environment. EVs must first and foremost be safe and reliable, and must operate with acceptable costs. Unfortunately, thus far, few kinds of batteries can meet all the requirements for EVs.[1–8] In the case of lithium-ion batteries, their use in EVs is still handicapped by significant safety problems, although their other performance attributes are often satisfactory. The main problem is that they use flammable organic electrolytes, which cannot withstand improper use, such as overcharging or short-circuiting, although much effort has been expended in this direction.[4] The development of new types of "green" battery materials and safer, less-expensive rechargeable systems is therefore necessary.

In the mid 1990s, a new type of rechargeable lithium-ion battery with an aqueous electrolyte was reported.[9,10] This battery uses lithium-intercalation compounds such as $LiMn_2O_4$, $LiNi_{0.81}Co_{0.19}O_2$, and VO_2 as the electrode material and an alkaline or neutral aqueous electrolyte,[9–11] and can overcome the disadvantages of nonaqueous lithium-ion batteries, such as high cost and safety problems. However, since its cycling was reported to be very poor it failed to attract strong interest from researchers.

Here we report that an aqueous rechargeable lithium battery (ARLB) with $LiCoO_2$ as the positive electrode, LiV_3O_8 as the negative electrode, and saturated $LiNO_3$ solution as the electrolyte shows good cycling and therefore shows promise as a power source for safe EVs.

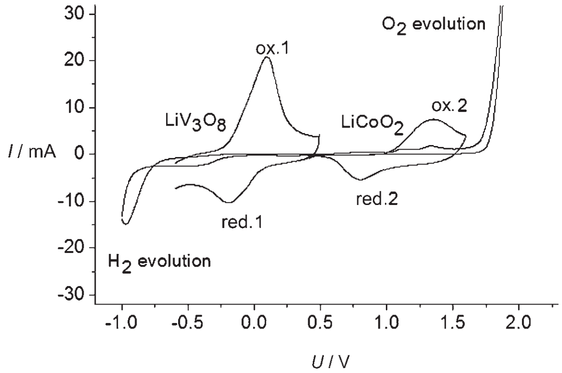

Figure 1. Cyclic voltammograms of LiV_3O_8 and $LiCoO_2$ in a saturated aqueous $LiNO_3$ electrolyte at a scan rate of 2 mVs^{-1}. An SCE was used as the reference electrode and a nickel pellet as the counter electrode.

The cyclic voltammograms of LiV_3O_8 and $LiCoO_2$ in saturated $LiNO_3$ aqueous electrolyte are shown in Figure 1. In the case of LiV_3O_8, there is one pair of redox peaks located at -0.19 (red. 1) and 0.098 V (ox. 1) versus a saturated calomel electrode (SCE), which is evidently due to the intercalation and deintercalation reaction accompanying gain and loss of an electron. The average redox potential is -0.046 V (versus SCE). Since hydrogen evolution was observed at a more negative potential due to overpotential (ca. -1.0 V versus SCE), it is clear that LiV_3O_8 is very stable in this aqueous electrolyte and can be used as a negative electrode material without significant hydrogen evolution. $LiCoO_2$ also exhibits one pair of Li^+ intercalation and deintercalation peaks at 0.8 (red. 2) and 1.35 V (ox. 2) versus SCE, respectively (average redox potential of 1.075 V versus SCE). These voltages are also lower than that for oxygen evolution, which is at approximately 1.8 V versus SCE. This illustrates that the positive electrode is also stable in this aqueous solution.

The charge and discharge curves of LiV_3O_8//$LiCoO_2$ cells in the first cycle in organic and aqueous electrolytes at voltages between 0.5 and 1.5 V are shown in Figure 2. The charge and discharge curves are similar in both cases, except that the capacity in the former is lower than that in the latter. The discharge capacity in aqueous and organic electrolyte is 55 and 88 $mAhg^{-1}$, respectively. The reason for this large difference in capacity requires further investigation, although it could be due to the cutoff voltage range. However, these results clearly show that the charge and discharge behavior in organic electrolytes can be transferred into aqueous solution if the intercalation and deintercalation voltages are within the stable electrochemical window of water.

It is clear that lithium ions deintercalate from $LiCoO_2$ and intercalate into LiV_3O_8 during the charge process and that during the discharge process the opposite occurs, that is, lithium ions deintercalate from LiV_3O_8 and intercalate into $LiCoO_2$. The average output voltage of this ARLB is

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[**] Financial support from the Shanghai Science & Technology Committee (04QMX1406) is greatly appreciated.

Supporting Information for this article is available on the WWW under http://www.angewandte.org or from the author.

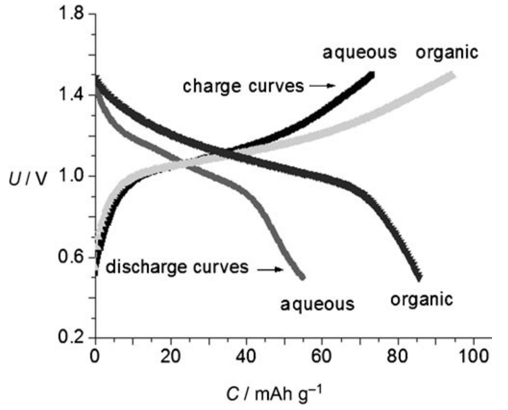

Figure 2. Charge and discharge curves of LiV_3O_8//$LiCoO_2$ cells in the first cycle in organic (1 M $LiPF_6$ solution in 1:1:1 (v/v/v) EC/DMC/DEC) and aqueous electrolytes at a voltage (U) between 0.5 and 1.5 V. The charge/discharge current density was kept constant at 0.2 mA cm^{-2} and the capacity (C) was calculated based on the weight of the positive electrode. EC = ethylene carbonate, DMC = dimethyl carbonate, DEC = diethyl carbonate.

approximately 1.05 V, which is a little lower than the results from the cyclic voltammetry $(1.075-(-0.046)=1.121\ \text{V})$ owing to overpotential. This average output voltage is similar to those of Ni–MH and Ni–Cd rechargeable systems (ca. 1.2 V). Since this voltage is also similar to that of primary Zn-MnO_2 batteries, they are also prime candidates for substitution. If the capacity of $LiCoO_2$ can be brought up to the level in lithium-ion batteries by adjusting the experimental conditions, its capacity density will be quite attractive.

During cycling at lower rate (0.2 mA cm^{-2}, ca. C/17 (C = charge/discharge rate)), the capacity of the LiV_3O_8//$LiCoO_2$ cells in the first few cycles in the aqueous electrolyte is very stable (see Supporting Information). Figure 3 shows the cycling behavior at 1 C between 0.5 and 1.5 V. Approximately 65 % of the maximal discharge capacity is maintained after 40 cycles, and approximately 36 % after 100 cycles. It is clear that this cycling behavior is much better than those reported previously.[9–11] Of course, its capacity still fades. However, we think that this capacity fading can be ameliorated by adjusting the composition of the electrolytes and the current collector and processing, since the data in Figure 1 clearly show that the side reaction from water is very slight. The choice of positive electrode is also very important since there is another small oxidation peak at 1.1 V in the enlarged cyclic voltammograms of $LiCoO_2$ shown in Figure 1.

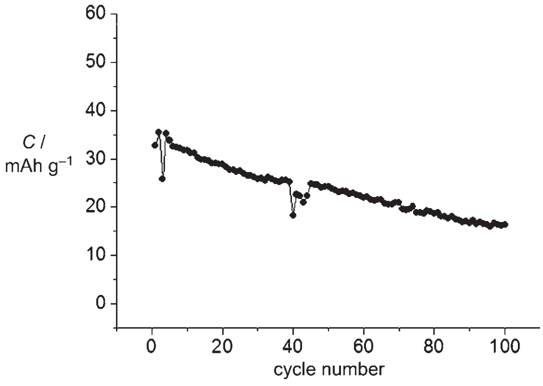

Figure 3. Cycling behavior of the LiV_3O_8//$LiCoO_2$ ARLB at 1 C; voltage range: 0.5–1.5 V. The discontinuities in the curve resulted from the shut-down of the power supply during the experiment.

In summary, an aqueous rechargeable lithium battery (ARLB) has been constructed with $LiCoO_2$ as the positive electrode and LiV_3O_8 as the negative electrode. It is an interesting alternative battery in light of its cost (inexpensive materials and easy assembly), environmental friendliness, and fundamental safety, and it avoids the use of poisonous metals and flammable and harmful acidic or alkaline electrolytes. Both electrode materials are stable in saturated aqueous $LiNO_3$ solution. Its average output voltage is approximately 1.05 V. Of course, further research is needed to improve the electrochemical properties, such as capacity, energy density, and cyclability. However, this approach provides another way to construct viable and practical rechargeable aqueous batteries by selecting intercalation compounds as positive and negative electrodes. Further studies are underway to determine the changes at the electrodes and the redox kinetics during the charge and discharge processes. The aqueous electrolyte used herein is better suited to a high rate capability for cells because the ionic conductivity of aqueous solutions is usually on the order of two orders of magnitude higher than that of nonaqueous electrolytes.[3] Further research in this area is also underway.

Experimental Section

Crystalline LiV_3O_8 and $LiCoO_2$ were prepared by a conventional solid-state reaction by heating a stoichiometric mixture of Li_2CO_3 and V_2O_5, or Li_2CO_3 and Co_3O_4, at 680 or 800 °C, respectively. The resulting products were cooled to ambient temperature to produce brown or black solids, respectively, which were investigated by X-ray diffraction.

The preparation of the negative and positive electrodes was conducted in a similar way. The electrode was prepared by pressing a powdered mixture of the sample, acetylene black, and poly(tetrafluoroethylene) in a weight ratio of 80:10:10. The positive and negative electrode disks were pinched into nickel meshes and immersed in a saturated $LiNO_3$ solution with an electrode separation of approximately 1 cm.

Cyclic voltammetry was performed with a three-electrode electrochemical cell in saturated $LiNO_3$ solution. An SCE and a nickel mesh were used as reference and counter electrodes, respectively.

Galvanostatic discharge and charge tests were performed with a cycle tester from LAND Electronic Co. controlled by a personal computer at a constant current density with a cutoff voltage of 1.5–0.5 V.

The electrochemical performance of the LiV_3O_8//$LiCoO_2$ cell was also tested in nonaqueous solution. This cell was assembled in an argon-filled glove box and used 1 M $LiPF_6$ in 1:1:1 (v/v/v) EC/DMC/DEC as electrolyte and Celgard 2400 as separator.

All electrical measurements were performed at ambient temperature.

Received: September 9, 2006

Keywords: battery materials · cyclic voltammetry · intercalations · lithium · redox chemistry

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