Electrochemical behavior of LiCoO$_2$ as aqueous lithium-ion battery electrodes

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ABSTRACT

Despite the large number of studies on the behavior of LiCoO$_2$ in organic electrolytes and its recent application as a positive electrode in rechargeable water battery prototypes, a little information is available about the lithium intercalation reaction in this layered compound in aqueous electrolytes. This work shows that LiCoO$_2$ electrodes can be reversibly cycled in LiNO$_3$ aqueous electrolytes for tens of cycles at remarkably high rates with impressive values specific capacity higher than 100 mAh/g, and with a coulomb efficiency greater than 99.7%. Stable and reproducible cycling measurements have been made using a simple cell design that can be easily applied to the study of other intercalation materials, assuming that they are stable in water and that their intercalation potential range matches the electrochemical stability window of the aqueous electrolyte. The experimental arrangement uses a three-electrode flooded cell in which another insertion compound acts as a reversible source and sink of lithium ions, i.e., as the counter electrode. A commercial reference electrode is also present. Both the working and the counter electrodes have been prepared as thin layers on a metallic substrate using the procedures typical for the study of electrodes for lithium-ion batteries in organic solvent electrolytes.

1. Introduction

Lithium intercalation into some high potential lithium-ion battery electrodes can occur in water, as well as in organic solvent electrolytes. An important criterion is that the intercalation potential range lies within the electrochemical stability window of the aqueous electrolyte. A critical factor is the value of the pH, for the potential range within which water is stable depends upon that factor [1].

The potential of the standard hydrogen electrode (SHE) is 3.045 V above that of pure lithium. However, the reversible hydrogen electrode (RHE), which is the theoretical value below which hydrogen gas should evolve from water, decreases from the SHE at a rate of 0.059 V per pH unit. The theoretical upper stability limit of water, above which oxygen should evolve, is 1.23 V above the RHE value, and therefore is also pH-dependent.

In practical situations, however, water decomposition seldom occurs at its theoretical limits. The electrochemical community speaks of over-potentials, with oxygen evolution from water not occurring at measurable rates until excess potentials of the order of 350–400 mV are reached [2].

On the other hand, the potentials of lithium battery electrode materials are referenced to the lithium potential, which is pH-independent. Thus, they are also pH-independent.

In principle, materials that are outside the stability range of water will tend to cause it to decompose. Positive electrode reactants that contain lithium and have potentials above the limit of water stability will react with water, absorbing lithium with the concurrent generation of protons. This will tend to decrease the pH of the water. It will not occur if their potentials are within the stability range of water.

Fig. 1 shows both the theoretical water stability range, and its pH dependence, generally known as a Pourbaix diagram, and the operating potentials of a number of lithium battery electrode materials in the general manner presented in Refs. [3,4].

There were several investigations of the possibility of the use of lithium reactant electrodes in aqueous electrolytes during the 1990s [3–6]. This approach has several obvious potential advantages over organic solvent electrolyte lithium batteries, including greater safety and low cost. Other possible features might potentially be high rate operation, better reversibility and extended cycle life. On the other hand, the lower potential range of water put a limit upon the possible cell voltage.

Water is cheaper than the organic solvents, inexpensive water-soluble salts are available, as are separators. In addition, the ionic conductivity of aqueous electrolytes is generally significantly greater than that of the organic electrolytes, allowing higher rates and lower voltage drops due to electrolyte impedance.

Much of the early work on lithium reactants in water electrolytes involved the use of LiMn$_2$O$_4$ as the positive electrode, and the combination of LiMn$_2$O$_4$ and VO$_2$ produced very attractive

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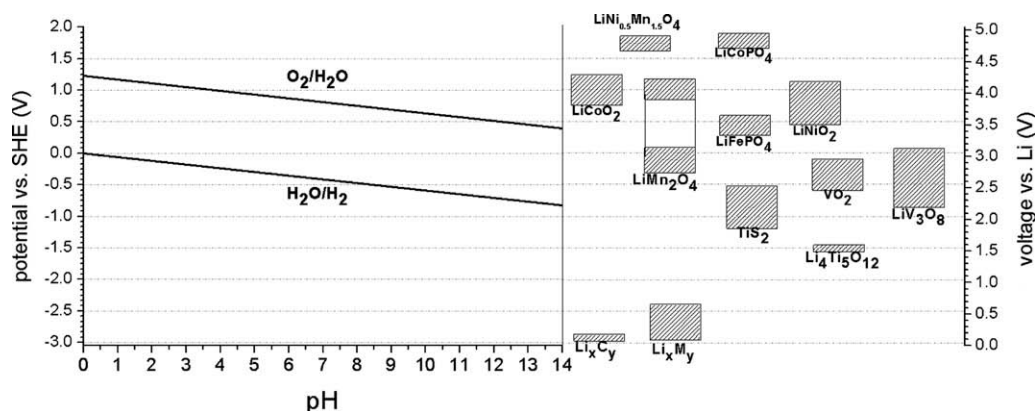
Fig. 1. Electrochemical stability window for water and lithium reaction potentials for several materials in lithium-ion batteries.

results. Subsequently, there have been several investigations in which $LiCoO_2$ was investigated as a potential positive electrode reactant in aqueous electrolyte systems [7–10]. As can be seen in Fig. 1, its operating potential range in organic electrolyte cells is not far from that of $LiMn_2O_4$. It has a relatively flat potential profile, high charge/discharge efficiency, a rather good cycle life, and attractive specific power properties in organic solvent electrolytes, and is used in a number of commercial batteries.

But in none of the available publications were the properties of $LiCoO_2$ in aqueous electrolytes particularly favorable. For example, the initial discharge capacity in a saturated $LiNO_3$ electrolyte was reported to be only 35 mAh/g at a 1 C rate, and it fell significantly upon cycling, becoming less than 20 mAh/g after 100 cycles [8]. In another paper [9], the initial value was 60 mAh/g at a current density of 0.2 mA/cm^2, and fell to about 40 mA/cm^2 after 12 cycles. These are significantly lower than what is typically found in organic solvent electrolyte cells.

Contrary to the prior work, the experiments reported here show that $LiCoO_2$ can have very attractive properties in an aqueous electrolyte under favorable conditions.

As has been shown elsewhere, water is stable over a much wider potential range than expected from its thermodynamic properties in aqueous solutions of $LiNO_3$. Cyclic voltammetric experiments with a nickel electrode showed a span of about 2.4 V [9], and this has been verified in our laboratory using a stainless steel electrode. We have observed stability up to about 1.6 V above the SHE in 1 and 5 molar solutions of $LiNO_3$, where the pH is 7. The theoretical limit at that pH is only 0.817 V. Thus, it is clear that positive electrodes with potentials as high as 4.6 V vs. Li should be stable in this aqueous solution.

This means that the use of such electrolytes can provide an inexpensive and simple tool for preliminary investigations of possible high potential lithium battery reactants, as was pointed out by Eftekhari [10].

2. Experimental

Commercial $LiCoO_2$ powder was obtained from Aldrich (99.8% purity) and no further treatment was performed. Working electrodes (WEs) were prepared by mixing $LiCoO_2$ powders with carbon black and an organic binder (PVDF), in a weight ratio of 80:10:10 in NMP (n-methyl pyrrolidone), also from Aldrich. After stirring, the mixture was deposited on stainless steel foil (type 304) by dipping, and then dried at 100 °C for 1 h. The electrode area was about 1.0 cm^2, and the weight of active material was typically in the range 3–5 mg for each sample.

Electrochemical characterization was performed by the use of both cyclic voltammetry (CV) and galvanostatic cycling with po-

tential limitation (GCPL) using Autolab PGSTAT100 and Biologic VMP3 instruments, respectively. All the measurements in $LiNO_3$ (from 0.1 to 5 M) aqueous electrolytes were made in a beaker cell using a double junction Ag/AgCl (3 M KCl), a reference electrode. For convenience, all potentials will be reported vs. the standard hydrogen electrode (SHE). The counter electrode (CE) was a slightly larger $Li_{0.5}Mn_2O_4$ layer in the same electrolyte compartment. This was prepared by delithiation of $LiMn_2O_4$ in 5 M $LiNO_3$. X-ray diffraction measurements were performed on the electrode layers using a PANalytical X'Pert diffractometer with Cu Kα-radiation. The cell parameters were refined in the rhombohedral system using the R-3m space group.

3. Results and discussion

It was mentioned earlier that we investigated the electrochemical stability window of aqueous electrolytes containing $LiNO_3$. They all showed a lack of decomposition up to about 1.6 V vs. the SHE.

To understand the electrochemical behavior of $LiCoO_2$ in the lithium nitrate aqueous solutions, we first performed cyclic voltammetry experiments from 0.4 to 1.1 V vs. the SHE using aqueous electrolytes containing different concentrations of $LiNO_3$, 0.1, 1.0 and 5.0 molar. This involved the use of a platinum counter electrode.

The results are shown in Fig. 2. The scan rate was rather low, 0.1 mV/s. In all cases, an electrochemical process was clearly observed, with current values several orders of magnitude higher
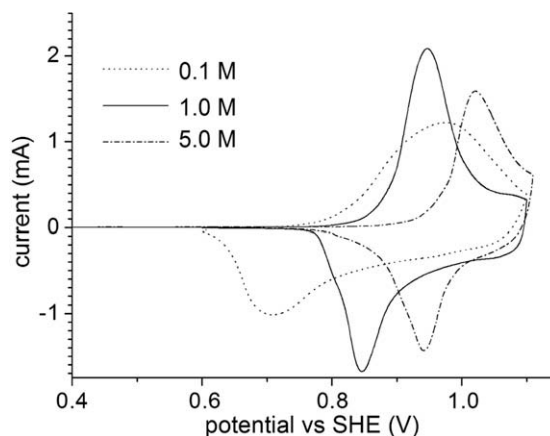

Fig. 2. Cycling voltammetry of $LiCoO_2$ electrodes at 0.1 mV/s in different $LiNO_3$ electrolytes.

than were found in the same potential range in the absence of active material. Especially at the higher concentrations, the current peaks were quite sharp, and the positions of the cathodic and anodic peak potentials were quite close. This indicates fast kinetics.

The potentials were consistent with those expected for the insertion and extraction of lithium in $LiCoO_2$ in organic solvent electrolytes. X-ray diffraction experiments were also performed upon samples below and above the current peak potentials when going in the positive direction, as well as after the negative current peak as the potential had returned to its original value. These results showed that the lattice parameter c had changed (from 15.3 to 15.8 Å) as the result of the positive current, and had returned to its original value (15.3 Å) after the reverse current peak. The lattice parameter changes were consistent with what is observed when lithium is removed, and then re-inserted into $LiCoO_2$ using organic solvent electrolytes.

Galvanostatic cycling experiments were undertaken to evaluate the behavior of $LiCoO_2$ in an aqueous electrolyte containing 5 M $LiNO_3$. A flooded three-electrode electrochemical cell was used for this purpose. It included the $LiCoO_2$ working electrode, an Ag/AgCl reference electrode and a large counter electrode of $Li_xMn_2O_4$. We believe that the use of this counter electrode, with a mass some 20 times that of the working electrode, and an initial composition about $Li_{0.5}Mn_2O_4$, rather than an inert material, was quite important. It allows the cell to cycle reversibly, whereas the use of some other possible counter electrodes, such as stainless steel, nickel mesh, or platinum foil, that have been used by others for experiments in water, is not fully reversible and can lead to a change in the composition of the electrolyte.

The potential range of these galvanostatic experiments was limited to 0.55–1.15 V above the SHE. This corresponds to the range in which the lithium concentration cycle from x equals 1.0–0.5 in Li_xCoO_2 in organic solvent electrolytes. One scan, from the 25th cycle, at a rate of 1 C is shown in Fig. 3. The potential is plotted both vs. SHE (left-axis) and vs. $Li_{0.5}Mn_2O_4$ CE (right-axis). Note that the experiments were designed to assess the reversibility of $LiCoO_2$ in an aqueous electrolyte, not to build a realistic cell. In that case the observed capacity was 105 mAh/g.

Experiments have been conducted which involved cycling such an electrode between these limits at a rate of 1 C. The results over 90 cycles are shown in Fig. 4a. Both the measured capacity and the Coulombic efficiency of each cycle are shown. It is interesting to see that the efficiency increased to very high values after the first few cycles, so that the measured capacity hardly changed at all.

Because of these very attractive results, the influence of the current upon the capacity during cycling was investigated. The results are shown in Fig. 4b. It can be seen that the Li_xCoO_2 electrode
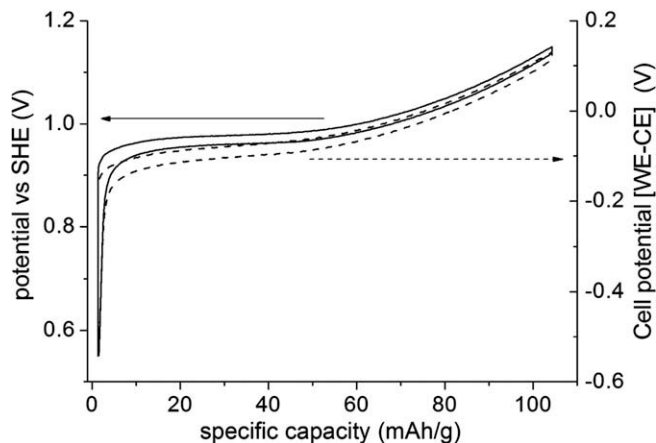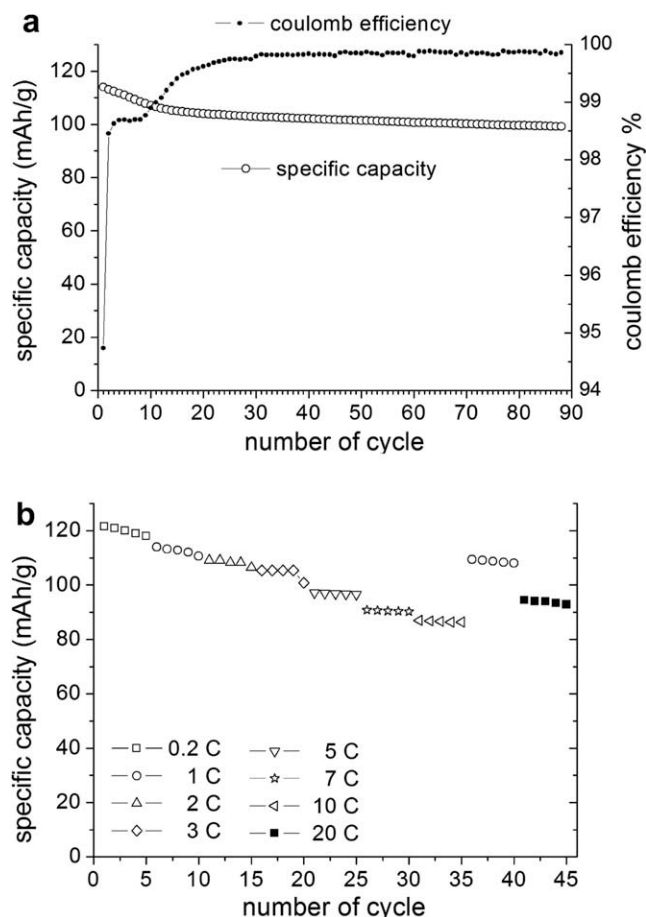

Fig. 4. Capacity trend vs. number of cycles at 1 C (a) and capacity trend vs. number of cycles at different rates. 20 C results were obtained by cycling the sample up to 1.35 V vs. SHE.

maintained an attractive capacity even to quite high rates in these aqueous electrolyte cells.

4. Conclusion

Lithium insertion and extraction can readily occur in $LiCoO_2$ in $LiNO_3$ aqueous solutions using a simple three-electrode cell with a reversible counter electrode. At salt concentrations of 5 M the kinetics become very fast, and the cycling behavior is very impressive, even at quite high rates.

Acknowledgment

References

[1] M. Pourbaix, in: Atlas of Electrochemical Equilibria, Pergamon Press, 1966.
[2] M.W. Kanan, D.G. Nocera, Science 321 (2008) 1072.
[3] W. Li, W.R. McKinnon, J.R. Dahn, J. Electrochem. Soc. 141 (9) (1994) 2310.
[4] W. Li, J.R. Dahn, J. Electrochem. Soc. 142 (6) (1995) 1742.
[5] W. Li, J.R. Dahn, D.S. Wainwright, Science 264 (1994) 1115.
[6] M. Zhang, J.R. Dahn, J. Electrochem. Soc. 143 (1996) 2730.
[7] Y.-g. Wang, J.-y. Luo, C.-x. Wang and Y.-y. Xia, J. Electrochem. Soc. A1425 (2006) 153.
[8] G. Wang, L. Fu, N. Zhao, L. Yang, Y. Wu, H. Wu, Angew. Chem. Int. Ed. 46 (2007) 295.
[9] G.J. Wang, N.H. Zhao, L.C. Yang, Y.P. Wu, H.Q. Wu, R. Holze, Electrochim. Acta 52 (2007) 4911.
[10] A. Eftekhari, Electrochim. Acta 47 (2001) 495.

Fig. 3. Charge/discharge of $LiCoO_2$ electrode at current rate of 1 C (25th cycle).