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Unusual overcharge tolerance behavior in gelled polymer lithium ion cells

Weibing Xing[*]

Electrochem-Canton, Division of Wilson Greatbatch Technologies, 100 Energy Drive, Canton, MA 02021 USA

Abstract

Unusual overcharge tolerance behavior was observed in Electrochem's polymer lithium ion cells. The cells could be overcharged up to several times the nominal capacity without a significant increase in cell potential. Experimental studies were carried out to understand this phenomenon. Cyclic voltammograms on gelled solid polymer electrolytes indicated that this phenomenon did not originate from an oxidation–reduction shuttle mechanism. A correlation between the apparent overcharge tolerance capability and anode to cathode capacity ratio was found. This observation suggested that the observed overcharge tolerance behavior was caused by non-dendritic lithium deposition on the carbon anode surface during overcharge. It was hypothesized that this lithium deposition created some weak electronic conducting paths through which part of the overcharge current was bypassed. Results of surface analyses on both fully charged and overcharged anodes were consistent with the above hypothesis. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In state of the art lithium ion cells, the cathode active materials commonly used are lithium transition metal oxides such as $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ or materials with mixed transition metals such as $LiNi_{1-x}Co_xO_2$. For reasons of chemical and electrochemical stabilities, the most commonly used cathode active material in commercial lithium ion batteries is $LiCoO_2$. The commonly used anode active materials are various types of carbons, e.g. coke and natural or synthetic graphite. For lithium ion cells based on these active materials, it is not desirable to overcharge the cells beyond a potential of about 4.2 V for the following reasons. Firstly, extra lithium ions will be extracted from the cathode. They will combine with electrons at the anode and deposit or plate on the carbon surface, since, for a balanced cell, the sites for lithium intercalation are already occupied. Deposited lithium may grow in the form of dendrites and may cause internal shorts. Secondly, the cell potential will increase fairly rapidly upon overcharge. Organic solvents commonly used in lithium ion cells, such as ethylene carbonate, dimethyl carbonate, diethyl carbonate and propylene carbonate, are not stable at high potentials. Therefore, overcharge of lithium ion cells will ultimately lead to accelerated exothermal

reactions and presents safety concerns [1]. For these reasons, commercial lithium ion batteries are often protected by electronic circuits to limit charge potentials. There are other overcharge protection methods such as the use of potential controlled polymerizable additives [2] and the use of suitable oxidation–reduction shuttle additives [3,4].

When subjected to overcharge tests, Electrochem's gelled polymer lithium ion cells showed an unusual behavior that allowed the cells to be overcharged up to several times the nominal capacity without a significant increase in cell potential. This observation prompted our investigation to understand the phenomenon. The experiments included cyclic voltammetry on the gelled solid polymer electrolyte, variations of anode to cathode capacity ratio and surface analysis. Results of these experiments led to possible explanations for the observed overcharge tolerance phenomenon.

2. Experimental

2.1. Preparation of gel polymer lithium ion and lithium cells

The technology for making gel polymer lithium ion cells/batteries was developed at Electrochem [5]. The anode was made by hot-pressing a mixture consisting of coke or graphite active material, carbon black, polyvinylidene

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[*] Tel.: +1-781-830-5838; fax: +1-781-575-1545.
E-mail address: wxing@greatbatch.com (W. Xing).

fluoride binder and a liquid electrolyte solution consisting of 1.4 M $LiPF_6$ in ethylene carbonate (EC)/propylene carbonate (PC) onto a copper foil. The cathode was made in a similar way with $LiCoO_2$ active material on aluminum foil. The gelled solid polymer electrolyte (SPE) was prepared by mixing three monomers having acryloyl functionalities, $LiPF_6$ and EC/PC plasticizers. Polymerization was initiated by thermal activation with benzoyl peroxide. A non-woven fabric was used in SPE to reinforce mechanical strength. The thickness of the SPE was about 51 μm. The anode/SPE separator/cathode assembly was stacked together and sealed in a foil/poly outer bag. All the cells had an active area of 25.5 cm^2. The coke anode was about 0.08 mm thick and the cathode was about 0.13 mm thick. The cell was about 0.74 mm thick and had a nominal capacity of 50 mAh. When the graphite anode was used, the cell was about 0.77 mm thick and had a nominal capacity of 60 mAh.

Polymer lithium cells were prepared by using lithium metal as the anode.

2.2. Overcharge test

Prior to the overcharge test, freshly prepared cells were cycled five times between 2.75 and 4.20 V at room temperature, at a 0.4 C rate. During overcharge testing, the cells were charged at 1 C for at least 6 h, as long as the cell potential was below a potential of 5 V. The cells were then discharged at 0.4 C to 2.75 V. For repeated overcharge testing, the cells were subjected to such an overcharge cycle for a number of times. All the overcharge tests were conducted at room temperature.

2.3. Cyclic voltammetry on SPE

Test cells were prepared by sandwiching the SPE between an aluminum foil and lithium metal or a copper foil, Al/SPE/Li or Cu. The Al foil was the working electrode. The Li metal or the Cu foil was the counter and reference electrode. The cell had an active area of 6.5 cm^2. An EG&G Potentiostat (273A) was used with 270/250 software. The potential was swept between 3 and 7 V at 10 mV/s for both anodic and cathodic scans.

2.4. Variation of anode to cathode capacity ratio

The anode to cathode capacity ratio $\gamma = (Q_a - Q_c)/Q_c$ expressed in percentage. Here Q_a is the reversible lithium intercalation capacity in the anode and Q_c is the cathode capacity at 4.2 V versus the carbon anode, corresponding to approximately $Li_{0.5}CoO_2$. Our balanced cells had a γ-value of 10%, i.e. 10% more anode capacity compared with that of the cathode. When γ-values were varied, Q_c remained constant while Q_a was either increased or decreased relative to a balanced value. In this study, γ-values were varied from −10 to 30%. The negative g-value means that the anode capacity is less than that of the cathode.

2.5. Surface analysis

Surface analyses on both fully charged and overcharged anodes were carried out using X-ray photoelectron spectrometry (XPS) and secondary ion mass spectrometry (SIMS), at the Center for Advanced Materials, University of Massachusetts, Lowell. The fully charged anodes were taken from cells charged to 4.2 V. The overcharged anodes were taken from cells charged for 6 h at 1 C. There was a brief exposure of the anodes to the air when they were taken out of the cells and then transferred to the antechambers of the spectrometers. Some anode samples were exposed to the air for an extended period of time, e.g. 1 day. For XPS, Li 1s spectra were measured within a depth of 20 Å from the sample surface. For SIMS, Li depth profile was measured. The samples were sputtered with Ga primary ions at an intensity of 10 keV and 0.5 nA. The maximum detection depth for the anodes was about 0.1 μm for 1 h sputtering.

3. Results and discussion

3.1. Observation of overcharge tolerance phenomenon

Fig. 1(a) shows the potential profile of a typical cell with a coke anode during an overcharge cycle. Upon charging, the cell potential reached 4.20 V in about 1 h, rose from 4.20 to 4.39 V in 17 min and then decreased slightly from 4.39 to 4.32 V in 19 min, forming a small peak-like feature at the initial stage of the overcharge. This was followed by a slow increase in cell potential over a period of 4.5 h when the cell was still being charged, demonstrating a plateau-like potential profile. At the end of the overcharge period (about 5 h), the cell potential was 4.55 V. The total charge capacity was six-fold of the nominal capacity. The cell, therefore, clearly demonstrated an unusual behavior towards overcharge. The discharge capacity immediately after the overcharge was 1.48 times the normal value, corresponding to approximately $Li_{0.25}CoO_2$. The time scale of the discharge period in Fig. 1(a) was normalized to that of 1 C rate so that direct comparison between the charge and discharge capacities could be made. In subsequent normal cycles, the cell delivered up to 98.5% of the capacity before overcharge. Clearly, the cell was not detrimentally affected by the abusive overcharge testing.

Fig. 1(b) shows the potential profile of a cell with a graphite anode during an overcharge cycle. The potential profile was similar to that of the cell with a coke anode. At the end of the 6 h charge, the cell potential was 4.71 V. The consequent discharge capacity was 1.48 times the normal capacity. This result indicated that the overcharge tolerance behavior was independent of the carbon type used in the anode.

To observe the overcharge behavior of cells with lithium anodes, polymer lithium cells were prepared and tested. Fig. 1(c) shows the potential profile of one such cell being
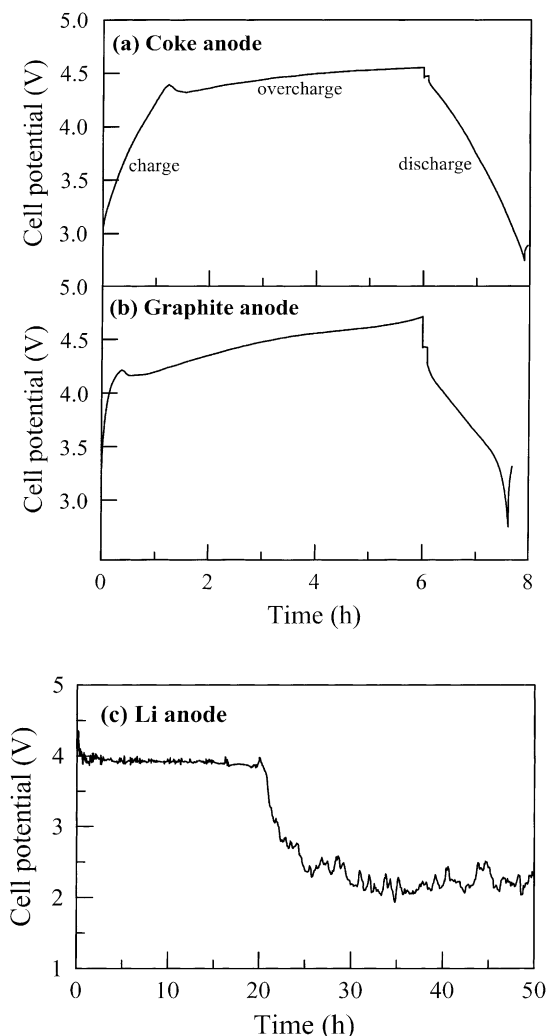
Fig. 1. Cell potential vs. time during an overcharge cycle for cells with (a) coke, (b) graphite and (c) Li anodes.

charged at 0.1 C rate. The cell potential remained around 4 V during charge with noisy features in the potential profile. After 20 h charge, the cell potential dropped suddenly from 4 to about 2 V and remained around this potential during the rest of the charge period. This behavior was likely caused by the formation of lithium dendrites on the lithium anode during charge.

Fig. 2 shows the potential profile of a cell with a coke anode during several overcharge cycles. The charge period in a cycle was 6 h for the first four cycles, corresponding to a charge capacity six-fold of the nominal capacity. At the end of charge, the cell potentials were 4.59, 4.65, 4.69, and 4.98 V for the first four overcharge cycles, respectively. After the first overcharge period, the cell was put on rest for 2 h. A small potential drop of 20 mV was observed during 2 h rest. The subsequent discharges gave 1.44, 1.36, 1.31, and 1.10 times the original capacity, respectively. During the fifth overcharge, the cell potential rose rapidly to 5 V within 1.3 h. The consequent discharge capacity was 1.04 times the original capacity. The potential drops, ΔV,
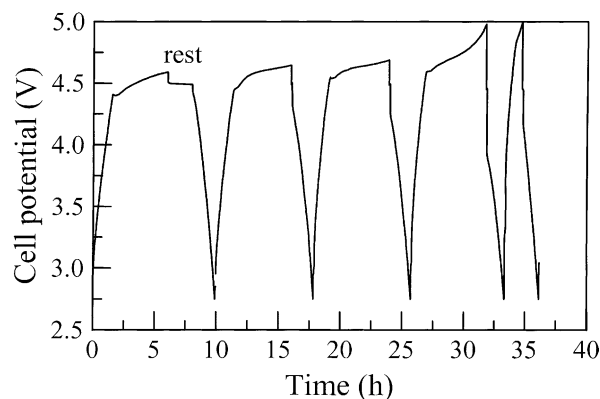

Fig. 2. Cell potential vs. time during repeated overcharges.

between overcharge and rest were 80, 127, 159, 415, and 507 mV for the five overcharge cycles, respectively. The increase in ΔV was due to an increase in cell impedance, which in turn, was due to both reduced crystallinity in Li_xCoO_2 [6] and growth of the solid electrolyte interphase layer [7] over repeated overcharges.

3.2. Cyclic voltammetry on SPE

Cyclic voltammetry (CV) on SPE was intended to observe any oxidation–reduction shuttle species. Fig. 3(a) shows a cyclic voltammogram of SPE versus lithium metal. In the anodic scan, the current remained nearly zero below 5.0 V. Around 5.5 V, an oxidation peak was seen. Only after 6.5 V did the current increase rapidly. On the reverse scan (cathodic scan), no peak was observed. This indicated that the anodic peak at 5.5 V was due to irreversible oxidation of the SPE. Fig. 3(b) shows CV of SPE versus Cu. The I–V curve was similar to that in Fig. 3(a), except that the oxidation peak occurred at a higher potential of 6.2 V. The current density in both cyclic voltammograms was much smaller than that
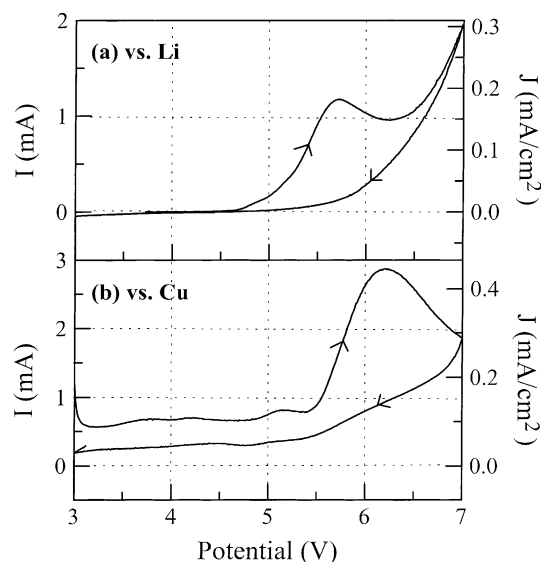

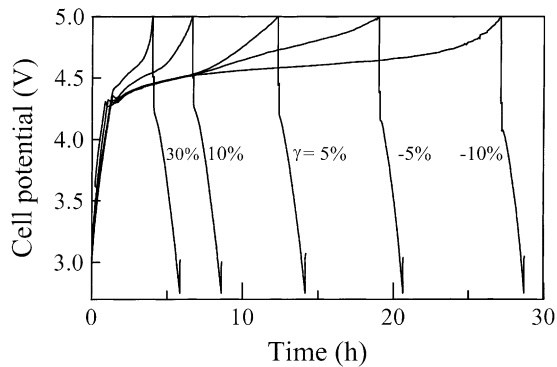Fig. 3. Cyclic voltammograms of (a) SPE vs. Li metal and (b) SPE vs. Cu.

Fig. 4. Cell potential vs. time during an overcharge cycle for cells with different *g*-values indicated.

during overcharge (≤ 0.1 mA/cm^2 versus 1.6 mA/cm^2). The CV data showed that there was no oxidation–reduction reaction in the SPE when the cell potential was less than 5 V during overcharge.

3.3. Effect of anode to cathode capacity ratio on overcharge behavior

Fig. 4 shows the potential profiles of cells with different γ-values, ranging from -10 to 30%, during an overcharge cycle where overcharge was continued until the cell potential reached 5 V. The cells all had coke anodes. The potential profiles clearly showed a pattern where overcharge duration or lengths of overcharge plateaus varied with different γ-values. Specifically, the lengths of the overcharge plateaus (including about 1 h normal charge) in Fig. 4 were 4.0, 6.6, 12.3, 19.0, and 27.1 h for the cells which had the γ-values of 30, 10, 5, -5, and -10%, respectively.

3.4. Surface analysis

Fig. 5(a) and (b) show XPS spectra for fully charged and overcharged anodes, respectively. The peaks around 58 eV
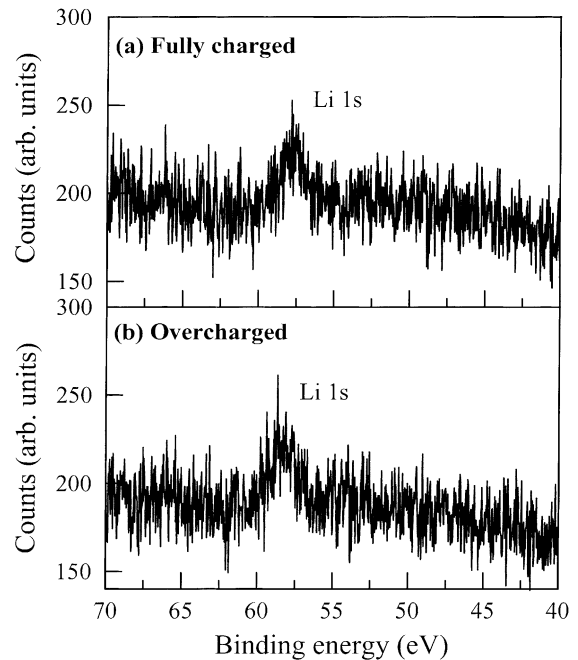

Fig. 5. XPS spectra for (a) fully charged and (b) overcharged anodes.

in both of the spectra were attributed to Li 1s of lithium compounds, reaction products of lithium with air. At the detection depth of ≤ 20 Å, the Li 1s peaks had the same intensity. Apparently, at this detection depth, XPS Li 1s spectra could not be used to distinguish between the two types of anodes.

Fig. 6 shows SIMS Li depth profiles for the fully charged and the overcharged anodes, as indicated. The anodes in Fig. 6(a) and (b) were exposed to the air for about 30 s. The anodes in Fig. 6(c) and (d) were exposed to the air for about 1 day. The sputtering time was proportional to the detection depth, about 0.1 μm maximum. The SIMS spectra showed the following patterns. (a) The overcharged spectra had additional sharp peaks near the surface, compared with
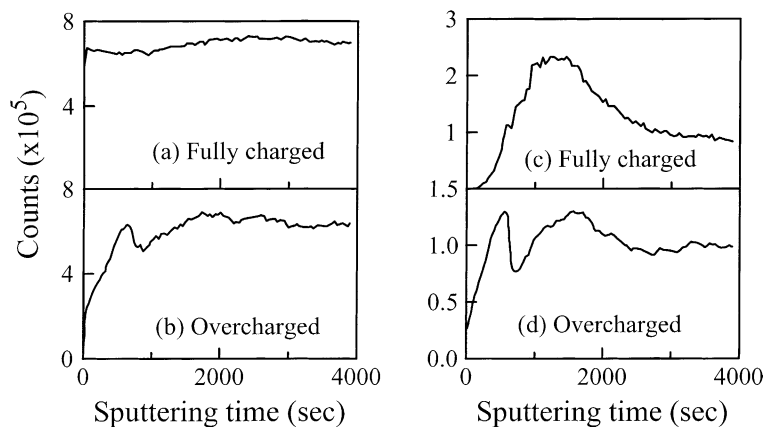

Fig. 6. SIMS Li depth profiles for fully charged and overcharged anodes, as indicated. The anodes were exposed to the air for (a and b) about 30 s and (c and d) about 1 day.

the fully charged. (b) Away from the surface, the patterns in the overcharged spectra were similar to those in the fully charged. (c) The fully charged spectrum with 30 s air exposure (Fig. 6(a)) was nearly flat, whereas the one with 1 day air exposure (Fig. 6(c)) showed a broad peak.

These patterns may be interpreted as follows. (a) The additional sharp peaks were likely due to deposited lithium on the anode surface. (b) This similarity further supported the assumption that lithium deposited only on the carbon surface during overcharge. (c) The flat Li depth profile represented intercalated lithium in the carbon. The broad peak feature was associated with reaction products of lithium with, e.g. oxygen and water in the air. The same was true for the sharp peak feature.

3.5. Mechanism of the unusual overcharge tolerance behavior

The above experimental observations suggested the following explanations for the observed overcharge tolerance behavior. When the gelled polymer lithium ion cells were overcharged, lithium would deposit or plate on the anode surface. This lithium deposition apparently did not form dendrites as evidenced by the smooth potential profiles of the cells during overcharge, compare Fig. 4 with Fig. 1(c). The fact that the cell potential leveled off at the initial stage of the overcharge implied that part of the overcharge current was bypassed by some weak electronic conducting paths. The observed pattern in Fig. 4 suggested that this weak electronic conducting path might be formed as a result of the non-dendritic lithium deposition on the carbon anode surface during overcharge. This scenario was more likely when highly porous separators, such as the SPE, were used.

Although the overcharge tolerance behavior could significantly delay the damage done by the overcharge, this feature may not be used as the only component for overcharge protection in gelled polymer lithium ion cells, due to the upward overcharge potential profile. Moreover, experiments showed that the length of the overcharge plateau was shortened when cells were constructed with multiple layers.

4. Conclusions

Gelled polymer lithium ion cells with highly porous SPE separators could have unusual overcharge tolerance behavior. Cyclic voltammetry study indicated that there was no oxidation–reduction shuttle species in the gelled polymer electrolyte. A close relationship between the apparent overcharge tolerance capability and anode to cathode capacity ratio was found. This observation suggested that part of the overcharge current was bypassed via some weak electronic conducting paths which were formed as a result of non-dendritic lithium deposition on the anode surface during overcharge. Observations from surface analyses on both charged and overcharged anodes were consistent with the above explanation.

Acknowledgements

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