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Rechargeable LiNiO₂/Carbon Cells

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ABSTRACT

Rechargeable cells can be made using two different intercalation compounds, in which the chemical potential of the intercalant differs by several eV, for the electrodes. We discuss the factors that play a role in the selection of appropriate lithium intercalation compounds for such cells. For ease of cell assembly the cathode should be stable in air when it is fully intercalated, like LiNiO₂. For the anode, the chemical potential of the intercalated Li should be close to that of Li metal, like it is in Li₂C₆. We discuss the intercalation of Li in LiNiO₂ and then in petroleum coke. Then, we show that LiNiO₂/coke cells have high energy density, long cycle life, excellent high-temperature performance, low self-discharge rates, can be repeatedly discharged to zero volts without damage, and are easily fabricated. In our opinion this type of cell shows far more promise for widespread applications than traditional secondary Li cells using metallic Li anodes.

Rechargeable Li batteries like Li/MnO₂ (1) have several advantages over conventional secondary systems like NiCad or new technologies like Ni-metal hydride. Secondary Li cells promise higher energy, higher voltage, and longer shelf life than competitive technologies (2). However, secondary Li batteries also have numerous disadvantages which may preclude their widespread acceptance in the marketplace.

Secondary Li batteries generally have a lower cycle life than NiCad cells. This results from the inability of attaining 100% Li cycling efficiency. Even in commercial Li/MoS₂ cells (3) there is a three-to fourfold stoichiometric excess of Li compared to that needed to fully intercalate the cathode. If the Li cycling efficiency is 99%, then 1% of the cycled Li is lost on each cycle. Therefore, to obtain 200 deep discharge cycles, at least a three-fold excess of Li is required.

The excess Li in these cells can cause other problems if the cells are allowed to discharge to low voltages outside their normal operating range. Many intercalation cathodes decompose (e.g., to form Li₂S or Li₂O) if allowed to react with excess lithium (4). The cells are then only poorly rechargeable because of irreversible chemical and structural changes in the cathode. In addition, the reactions that occur at low voltage can often totally consume the Li anode, making charging difficult.

The relatively poor cycling efficiency of the Li anode arises because it is not thermodynamically stable in typical nonaqueous electrolytes. The surface of the Li is covered with a film of the reaction products between the Li and the electrolyte (5, 6). Every time the Li is stripped and plated, some new Li surface is exposed and hence passivated, consuming Li. Much effort has been expended to improve the cycling efficiency of the Li anode through changes to the electrolyte (7, 8) or through the application of uniaxial pressure to the Li surface (9, 10). Practical cells use both optimum electrolytes and pressures of about 1.4 MPa on the Li electrode to achieve efficiencies of up to 99% (3). Special separators which can withstand high uniaxial pressures and which have a pore size smaller than the diameter of typical Li dendrites must be used in these cells. These separators, generally polypropylene or polyethylene microporous films, are relatively expensive and contribute significantly to the raw materials cost of a spiral

wound secondary Li cell. As long as Li metal anodes are used, the uniaxial pressure requirement precludes the construction of flat or prismatic cells with thin-walled cases.

Secondary Li cells with Li metal anodes require thin electrode technologies. Generally, the anode and cathode thicknesses are about 100 μm. Thin electrodes are required because: (i) The thickness of the stripped and plated Li deposit is proportional to the cathode thickness; electrode thicknesses are kept thin to minimize the risk of dendrite penetration of the separator during the plating of the Li. (ii) The conductivity of nonaqueous electrolytes are typically two orders of magnitude less than the aqueous electrolytes used in NiCad cells. To obtain reasonable rate capability, electrode separations and thicknesses must be roughly an order of magnitude less than in NiCad. The thin electrode technology, the excess Li, the need for assembly equipment to be located in dry rooms, and the relatively expensive separators all contribute to the relatively high cost of secondary Li cells compared to NiCad.

Secondary Li cells typically use recharge currents which correspond to C/10 (10 h for full recharge) rates (3). This is because the risk of dendrite penetration of the separators increases as the recharge current is increased and because the Li cycling efficiency is improved when the current density used for plating the Li is substantially less than that used for stripping (1, 3). This represents a major disadvantage for secondary Li cells since NiCad cells and Ni-metal hydride cells can be charged in one hour or less.

The safety of AA size secondary Li cells with metallic Li anodes is presently less than satisfactory (11, 12). There have been reported incidents of fires involving equipment powered by secondary Li/MoS₂ cells which led to a product recall (13, 14). There have even been similar recalls involving primary Li/MnO₂ cells (15) suggesting that safety is a central issue which must be resolved to make this a viable technology.

It is clear that although the use of metallic Li leads to higher energies, higher voltages, and longer shelf life than conventional cells, the many disadvantages of this technology severely limit its application. Here we show that cells using two different Li intercalation compounds, in which the chemical potential of the intercalated Li differs by several eV, for the electrodes eliminate most of the disadvantages discussed above while retaining the essential advantages of secondary Li cells. There is, of course, a

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small penalty to be paid in cell voltage and in cell energy. Cells of this design are often called "rocking chair cells" (16) because the Li shuttles or "rocks" between the electrodes as the cell is charged or discharged. At least one Japanese company announced its plans to commercialize this technology (17).

First we discuss the selection of appropriate materials for the electrodes of "rocking chair" cells and show that LiNiO_2 and petroleum coke are good candidates for the cathode and anode, respectively. Next, we review the electrochemical intercalation of Li in these two materials. Then we describe the construction of 1225 coin cells using LiNiO_2 and petroleum coke as electrode materials. The results of cycle testing these cells under a variety of conditions demonstrate that most of the disadvantages associated with secondary Li cells are eliminated. Finally, we summarize our work and comment on the key problems remaining in the further development of rocking chair cells.

Electrode Materials for "Rocking Chair Cells"

The voltage, V , of an electrochemical cell based on the intercalation of Li into a host electrode, relative to Li metal, is

$$V = -\mu/e \quad [1]$$

where μ is the chemical potential of the Li intercalated in the host and e is the magnitude of the electron charge (18). Normally, the voltage varies with the composition of the intercalation compound. Figure 1 shows the chemical potential ranges of intercalated Li in a variety of compounds. Clearly it is possible to find materials where the chemical potential differs by several eV.

In a practical rocking chair cell it is necessary to ensure that one of the electrodes is loaded with lithium prior to cell assembly. Most powdered intercalation compounds are pyrophoric when loaded with Li. However, the Li will not deintercalate to react with air or moisture if it is sufficiently tightly bound in the intercalation compound. When the chemical potential is less than about -3.5 eV, lithium intercalation compounds are generally observed by x-ray diffraction to be air stable. Fortunately, there are several well-known Li insertion compounds which have $\mu < -3.5$ eV even when the material is loaded with substantial Li. Of these, $\text{Li}_{1-y}\text{NiO}_2$ ($0 < y < 0.8$) (19, 20), $\text{Li}_{1-y}\text{CoO}_2$ ($0 < y < 0.8$) (21), and $\text{Li}_{1-y}\text{Mn}_2\text{O}_4$ ($0 < y < 1$) (22) are currently the most studied.

$\text{Li}_{1-y}\text{NiO}_2$ was selected for the cathode in our studies because it has a lower voltage vs. Li than either $\text{Li}_{1-y}\text{CoO}_2$ or $\text{Li}_{1-y}\text{Mn}_2\text{O}_4$. At sufficiently high voltages (generally greater

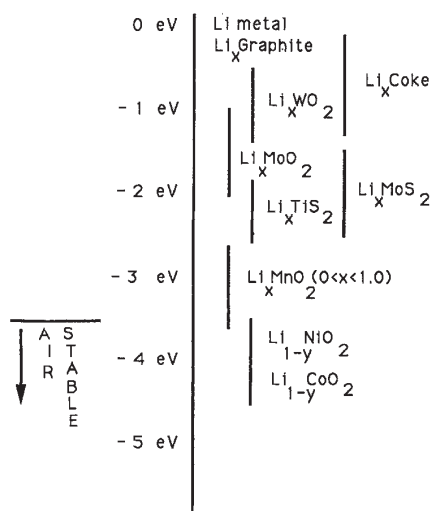


Fig. 1. Showing the chemical potential ranges of intercalated Li in a variety of compounds. Chemical potentials are measured relative to Li metal.

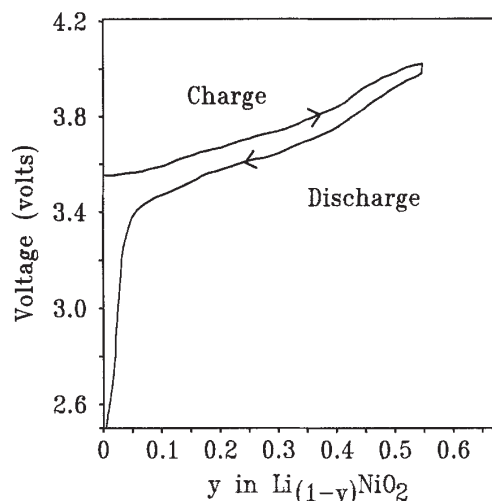


Fig. 2. Voltage of $\text{Li/Li}_{1-y}\text{NiO}_2$ cells vs. y for the first charge and discharge of the cell. The current was chosen so that a change $\Delta y = 1$ occurred in 40 h.

than 4.0 V) the oxidation of the nonaqueous electrolytes used in secondary Li cells can occur (23). This electrolyte oxidation is to be avoided if long cycle life cells are to be made. The voltage-composition profile for $\text{Li/Li}_{1-y}\text{NiO}_2$ cells is shown in Fig. 2. The cells cycle reversibly for $\Delta y = 0.5$ below 4.0 V.

The anode should be selected from those materials which have chemical potentials close to that of lithium metal. Of these, carbons like graphite and petroleum coke are especially well suited (24, 25). Graphite and petroleum coke can intercalate Li to composition limits of LiC_6 (corresponding to 0.37 Ah/g) and $\text{Li}_{0.5}\text{C}_6$, respectively (25). The voltage-composition profile for Li/petroleum coke cells is shown in Fig. 3. Li/graphite cells have a much "flatter" voltage-composition profile, which varies from about 0.25 V near $x = 0$ to about 0.70 V near $x = 1$ in Li_xC_6 (25). For reasons discussed below, we chose petroleum coke over graphite for our electrodes even though graphite gives twice the specific capacity.

In earlier studies of Li/graphite and Li/coke cells (24) we showed that during the first electrochemical intercalation of Li into carbon, some Li is irreversibly consumed. The

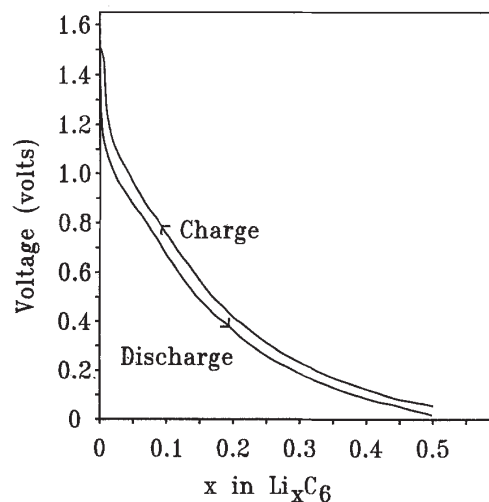


Fig. 3. Voltage of $\text{Li/Li}_x\text{C}_6$ cells vs. x for the second discharge and charge of the cell. The carbon in the positive electrode is petroleum coke. The current was chosen so that a change $\Delta x = 1$ occurred in 80 h.

amount of Li consumed was shown to be proportional to the surface area of coke electrodes, suggesting that a passivating film of constant thickness was being formed. In the case of graphite electrodes, there was additional irreversible consumption of Li. This was thought to be associated with electrolyte reduction occurring on fresh surfaces of graphite exposed during partial exfoliation of graphite caused by the intercalation of electrolyte solvent. Since the amount of Li in a rocking chair cell is entirely supplied by that initially loaded into the cathode, it is very important to minimize any possible loss of Li to film forming or other irreversible reactions. Therefore, we decided to use low surface area petroleum coke electrodes in our first cells.

Experimental

LiNiO₂ was prepared as outlined in Ref. (20). The material used in the 1225 coin cells had an actual stoichiometry of Li_{0.96}Ni_{1.04}O₂. Top premium petroleum needle coke designated XP was obtained from Conoco, Incorporated (Houston, Texas) in the form of lumps about 1 cm³. This material is about 99.5 weight percent (w/o) carbon with sulfur (0.3 w/o) as the major impurity. The spacing between carbon planes, *d*(002) = 3.46 Å is typical for needle cokes. The petroleum coke was ground and then sized using standard sieves. The coke used to fabricate electrodes was -200/+400 mesh (i.e., 75 μm > particle diameter > 38 μm).

Stainless steel 1225 coin cell hardware (12 mm outside diameter and 2.5 mm thickness) obtained from Rayovac Corporation (Madison, WI) was used. A polypropylene gasket is used to make the seal. Leak tests of coin cells filled only with dimethoxyethane (DME) (about 70 mg) showed no measurable weight loss (<0.1 mg) after 1 week at 55°C in a vacuum oven, proving that the leak rates at these temperatures are negligible.

Disk-shaped tablet electrodes were prepared from a mixture of the active powders with binder and carbon black followed by pressing. A laboratory scale rotary tablet press (Stokes 511) was used to press tablets with uniform thickness and mass. The tablet thickness and mass were adjusted so that: (i) The thickness of the tablets plus separator was equal to the inside height to the cell. Each tablet was approximately 1.0 mm thick. (ii) The masses are adjusted so that at the completion of the first charge of the cell the cathode stoichiometry is Li_{0.5}NiO₂ while the anode stoichiometry is simultaneously Li_{0.5}C₆. The calculation accounts for that Li irreversibly consumed by the carbon anode. Typical active masses for the LiNiO₂ and petroleum coke electrodes were 93 and 61 mg, respectively.

LiN(CF₃SO₂)₂ was obtained from 3M Corporation (Minneapolis, MN) and was dried under vacuum at 140°C before use. Typical electrolytes used in these cells were 1M solutions of this salt in a 50:50 mixture of propylene carbonate (PC) and DME or in a 50:50 mixture of ethylene carbonate and DME. We observed no difference in performance between cells using PC or EC as a cosolvent. PC and EC (Texaco) were purified by vacuum distillation. DME from Aldrich was used as received or was repurified from Li benzophenone ketyl solutions. Electrolytes were not used if the moisture content determined by Karl-Fisher titration exceeded 100 ppm.

Celanese No. 2502 microporous films were used as separators in most cells. In some cells we used nonwoven polypropylene separators and observed similar results. All cells reported here were assembled in a dry room with RH < 0.5%. Cells were charged and discharged using computer-controlled battery cyclers capable of constant current cycling between fixed voltage limits, constant capacity cycling, or discharge through a fixed load followed by a charging to a voltage cutoff. These chargers were designed and built at Moli Energy (1990) Limited.

Results and Discussion

Figure 4 shows the first cycles of a LiNiO₂/coke 1225 coin cell. During the first charge, Li is deintercalated from Li_{1-y}NiO₂ and is intercalated into Li_xC₆. The capacity of the first charge is about 18% larger than that of the subsequent cycles. The Li which has been consumed is thought to be now incorporated into the passivation film on the surface

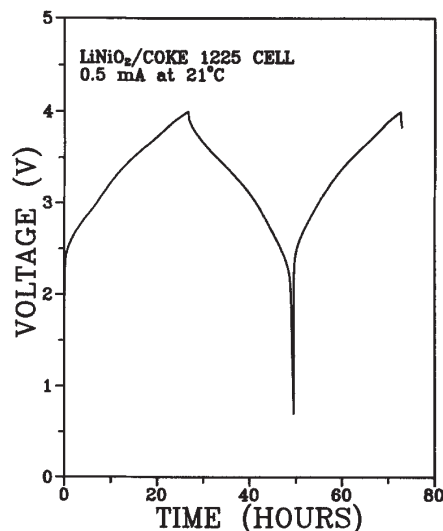


Fig. 4. First cycles of a LiNiO₂/coke 1225 coin cell at 21°C. The cell is charging and discharging between 3.9 and 0.7 V using a constant current of 0.5 mA.

of the intercalated coke (24) and is hence unavailable for the next discharge of the cell. The cell capacity on the second cycle is about 10 mAh when the cell is charged to 4.0 V. Figure 5 shows the capacity vs. cycle number for a cell at room temperature. On the scale of Fig. 5 the charge and discharge capacities are indistinguishable after the first cycle. Apart from a small amount of early capacity fade, these cells exhibit good reversibility. Since there is no excess Li in these cells, each Li atom lost to an irreversible reaction will be unavailable for cycling and capacity loss will result. The data in Fig. 5 prove that the intercalation of Li in Li_{1-y}NiO₂ and in Li_xC₆ is nearly 100% reversible. Once the capacity loss associated with the first charging of the cell has been eliminated, very little further loss is seen. At the time of this writing cells have been tested continuously for 11 months and show no sign of impending failure as evidenced by increases in charge or discharge overvoltages or by capacity loss.

These rocking chair cells have no excess Li in the anode or cathode, so they should be tolerant to repeated discharges to zero volts. At zero volts, all the available Li has been removed from Li_xC₆ and inserted into Li_{1-y}NiO₂. Figure 6 shows the voltage vs. time for cycles 10 and 11 and for

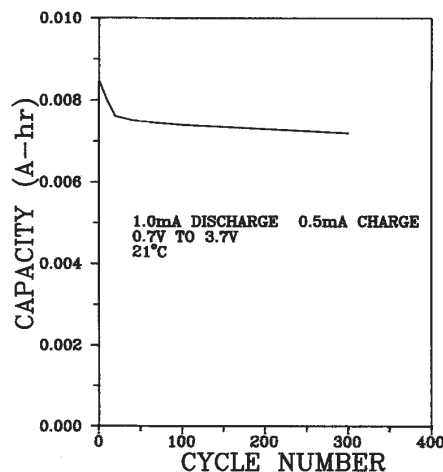


Fig. 5. Capacity vs. cycle number for LiNiO₂/coke 1225 coin cells cycled at 21°C using constant current (0.5 mA). The voltage limits are indicated in the figure.

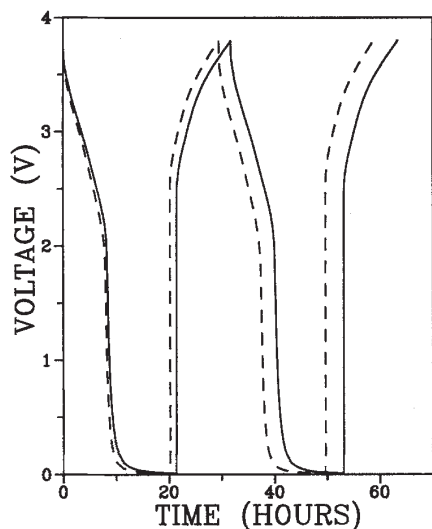


Fig. 6. Voltage vs. time for a LiNiO₂/coke 1225 coin cell discharged through a 3 kΩ load and then charged to 3.8 V. The 10th, 11th (solid), and 110th, and 111th (dashed) cycles are shown. The cell was at 21°C.

cycle 110 and 111 of a cell discharged through a 3 kΩ resistor and then charged to 3.8 V. The charge is initiated 10 h after the cell voltage drops below 0.1 V. Thus, the cell spends 10 h near zero volts on every cycle. Figure 7 shows the capacity fade for the cell of Fig. 6 and for an identical cell discharging through a 1 kΩ resistor. Both of these cells have cycled to zero volts hundreds of times without significant capacity loss. Again, at the time of writing these cells have been tested for 11 months with no signs of impending failure.

Figure 8 shows capacity vs. cycle number for 3 LiNiO₂/coke cells cycling at 55°C using a current of 1 mA for both charge and discharge. The rate of capacity loss increases when the upper voltage limit is raised, presumably because the electrolyte oxidation rate increases at the higher voltages. Nevertheless, the cell charged to 3.7 V shows excellent cycling behavior even at 55°C. At the time of this writing, the cell charging to 3.7 V has reached over 300 cycles and shows no signs of impending failure.

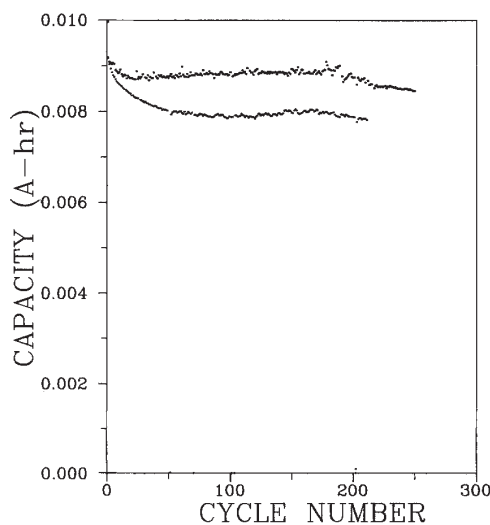


Fig. 7. Capacity vs. cycle number for LiNiO₂/coke 1225 coin cells discharged through 1 and 3 kΩ resistors. The lower capacity data are for the 3 kΩ load. The cell voltage remains below 0.1 V for 10 h before each recharge (see text).

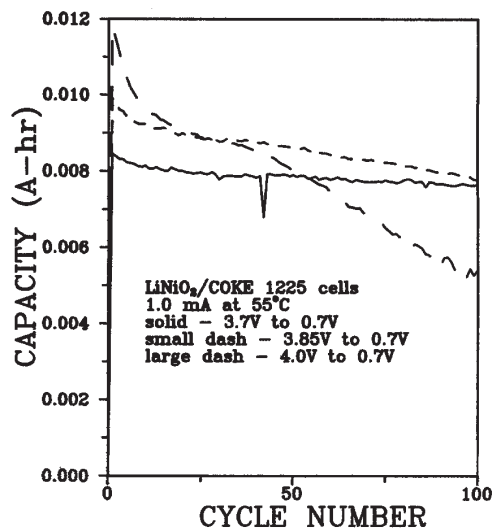


Fig. 8. Capacity vs. cycle number for LiNiO₂/coke 1225 coin cells cycled at 55°C. The cycling current was 1.0 mA. The voltage limits are given in the figure.

LiNiO₂/coke cells were discharged to a fixed capacity at 85°C and then recharged to 3.7 V. Figure 9 shows the voltage reached at the end of each constant capacity discharge plotted vs. cycle number for cells discharged to 1, 2, 4, and 6 mAh. The tests were stopped when the cell voltage reached 2.0 V. Over 1000 cycles were obtained for the 1 mAh discharge (10% DOD). These cells were weighed before and after testing and a small weight loss, corresponding to about 15% of the weight of the DME, was observed. The boiling point of DME is 85°C and the permeability of the polypropylene seal increases with temperature. Therefore it is likely that cell leakage contributed to the failure of the cells cycled at 85°C. The data in Fig. 9 proves the suitability of this chemistry for high-temperature applications.

The cells also show excellent storage properties. Figure 10 shows the capacity vs. cycle number for a cell charged to 3.9 V and stored for 30 days at room temperature after every ten cycles. After storage, the cells were discharged first. The first discharge after the storage period does not show appreciable capacity loss. The cells were cy-

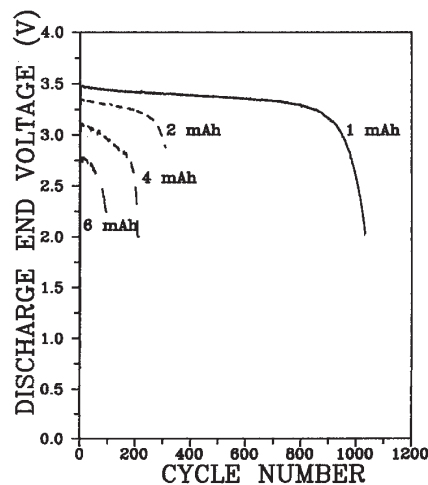


Fig. 9. End of discharge voltage vs. cycle number for constant capacity discharges (1.0 mA) at 85°C. The LiNiO₂/coke cells were charged to 3.7 V at 1.0 mA following each discharge. Four cells were tested using discharge capacities of 1, 2, 4, and 6 mAh.

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