

THE DEVELOPMENT OF LITHIUM RECHARGEABLE BATTERIES

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Summary

A brief overview of the development of lithium rechargeable batteries is presented. The cell system of Li//ethylene carbonate (EC)/2-methyltetrahydrofuran (2MeTHF)/LiAsF₆//amorphous V₂O₅-P₂O₅ showed long cycle life. This good performance is one example of the rapid development taking place in lithium rechargeable batteries. The rechargeable systems are progressing toward an advanced stage of development.

Introduction

Recent progress in the study of lithium rechargeable batteries has been very rapid: many studies are actively being conducted throughout the world [1 - 6]. It is quite possible that within 10 years, Ni-Cd batteries will begin to be replaced by lithium systems.

The most advanced cell systems are Li/MoS₂ and Li//2MeTHF/LiAsF₆//TiS₂. The cell construction technique is better developed in the case of Li/MoS₂. The advantage of Li//2MeTHF/LiAsF₆//TiS₂ lies in its excellent electrolyte properties [7]. Another promising cell system is that of Li//SO₂//CuCl₂ in view of its good rechargeability and high voltage [8]. Also, a Li//ethylene carbonate-mixed-solvent/LiAsF₆//amorphous V₂O₅-P₂O₅ system has been studied in our laboratory.

Although this paper focusses on the properties of cathode active materials and electrolytes for ambient-temperature cells, other improvements in the separator, anode, cathode fabrication, electrode packing, and cell construction are also necessary for the development of a practical cell.

Cathode active materials

Cathode active materials can be classified into inorganic and organic materials. Organic materials are the more interesting because of their light weight and high energy density [9], but their cycle time can be very short.

Metal phthalocyanines (MePc) are organic cathode-active materials that show a large specific capacity of around 1400 A h kg⁻¹ for the iron-based

compound. Unfortunately, some MePc with Fe, Co, Mn, Ni, Cr or Ag were found to act as catalysts for propylene carbonate decomposition during discharge [11]. For this reason, metal-free Pc(H₂Pc) is now being studied. The best specific capacity is 800 A h kg⁻¹, based on H₂Pc weight, obtained using a coin cell (23 mm dia., 2 mm thickness) with a Teflon-bonded cathode (active material in cathode = 70 wt.%) and a propylene carbonate(PC)/dimethoxyethane(DME)//LiClO₄ electrolyte. Although the cell had a large specific capacity, the actual capacity was only 45 mA h because of the low packing density. The same H₂Pc cell could be cycled 17 times from a 4.2Li/H₂Pc discharge depth. The poor rechargeability may be due to co-intercalation of ClO₄⁻ ions when the cell is recharged [12].

Recently, polyacetylene [13], polyaniline [14] and other polymer cathodes have been reported to show good properties. At present, the study of these properties is only at the fundamental stage: it will be many years before a practical cell will be achieved.

Various inorganic materials have been studied to determine their suitability as cathode active materials in rechargeable lithium cells. Some of those materials could be cycled more than 100 times, *e.g.*, see Fig. 1 [15 - 26]. In many cases, the lower limit of the discharge voltage is determined by the decomposition voltage of the electrolyte. Of these materials, Cu₂V₂O₇ [27] and amorphous V₂O₅-P₂O₅ (a-V₂O₅-P₂O₅) [28] are being studied in our laboratory.

Cycling studies of Li//2MeTHF/LiAsF₆//Cu₂V₂O₇ have been carried out under a 2 - 3.5 V charge-discharge at 0.5 mA cm⁻². The first discharge capacity was 295 A h kg⁻¹ (3.75Li/Cu₂V₂O₇). Around 0.5Li/Cu₂V₂O₇ could not be recharged. After 100 cycles, the capacity decreased to 246 A h kg⁻¹ (3Li/Cu₂V₂O₇), see Fig. 2. Unfortunately, the development of an

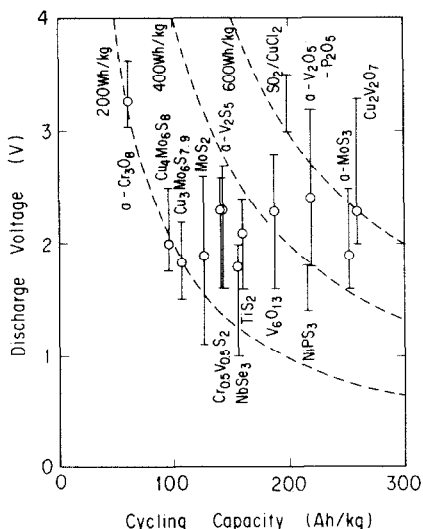


Fig. 1. Rechargeable cathode active materials.

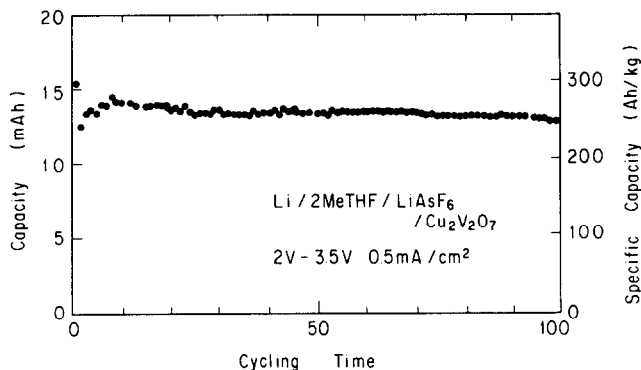


Fig. 2. Capacity change with cycling (Li/Cu₂V₂O₇ coin cell).

internal short in the 104th cycle terminated the test. X-ray diffraction analysis showed that copper metal had deposited on the cathode during cycling. It is possible that copper in Cu₂V₂O₇ is replaced by lithium during discharge; a similar process has been reported in a cell using Chevrel-phase material such as Cu₂Mo₆S_{7.75} [29].

Although V₂O₅ is a well-known cathode material, its rechargeability is poor [30]. Studies to determine whether the rechargeability of amorphous V₂O₅ cathodes could be improved began in November, 1982. The possibility of lithium intercalation in a glass of the V₂O₅-P₂O₅ system was pointed out initially in 1983 by Pagnier *et al.* [31, 32]. Unfortunately, they could not demonstrate any rechargeability of the V₂O₅-P₂O₅ glass. A fundamental study of V₂O₅ glass cathodes was also reported by Yamagata *et al.* [33]. Good rechargeability of a-V₂O₅-P₂O₅ cathode has recently been reported [28]; the specific capacity was more than 300 A h kg⁻¹ (>2Li/a-V₂O₅-P₂O₅) for a voltage between 4 V and 1 V, and the cell gave over 500 cycles of service. As in most cases, the limiting factor of cycling was the rechargeability of the lithium electrode.

Electrolytes

One method for improving anode charge/discharge efficiency is by the use of Li-alloy as an anode. Small coin cells with Li-alloy are commercially available in Japan. Although their capacities are very small, service lives are over 1000 cycles [34, 35]. In spite of these promising properties, Li-alloy has many short-comings. For example, it reduces the cell voltage and has poor volumetric efficiency. Since 1,3-dioxolane/LiClO₄ solutions have been found to be shock sensitive [36], the best electrolyte is 2MeTHF/LiAsF₆ [26]. 2MeTHF/LiAsF₆ has been reported to show very high "Figures of Merit" (FOM) for lithium electrode cycling; FOM is defined as: (total accumulated charge capacity)/(excess Li in the cell). The FOM of 2MeTHF/LiAsF₆ has been reported by the EIC group [7] to be ~30, but this electrolyte has the disadvantage of a low conductivity.

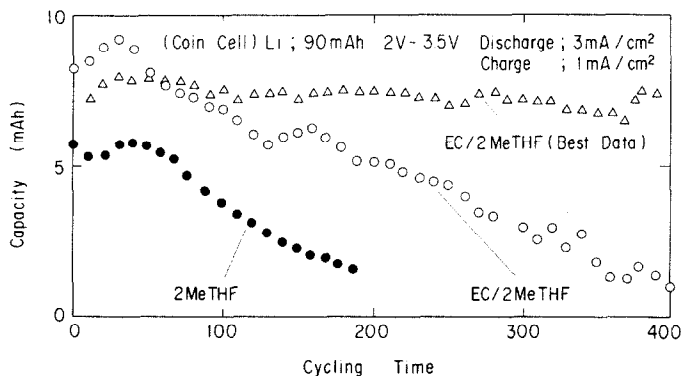


Fig. 3. Cycling properties of coin cells with EC/2MeTHF//LiAsF₆ electrolytes.

Ethylene carbonate (EC) mixed-solvent electrolytes [27, 37] have also been examined. When EC is mixed with low viscosity ether electrolytes, the resistivity decreases. This is because EC has a very high dielectric constant and therefore assists the dissociation of lithium salt in the solvent. Based on an earlier report [26] of the reactivity between lithium metal and PC, there may be some doubt over use of EC from the standpoint of lithium charge/discharge efficiency. EC also forms Li₂CO₃ on the lithium surface. However, it was thought that an EC mixed system would have potential for the following reasons:

(i) Usually, the donor number of EC is lower than that of ethers. This means that Li⁺ ions are selectively surrounded by ether molecules. Thus the lithium surface is covered with the reaction products of ethers rather than with Li₂CO₃ during cycling.

(ii) If the solute is LiAsF₆, it is possible that the protective film is not Li₂CO₃, but rather the reaction products of LiAsF₆.

Purification of the electrolytes was considered to be an effective means of improving the FOM in real cells. The results of the cycling tests are shown in Fig. 3. The cathode used was a-V₂O₅-P₂O₅. The cell was a coin cell of 23 mm dia. and 2 mm high. The best result was obtained when using a purified EC/2MeTHF//LiAsF₆ electrolyte. This cell could be cycled up to 600 times. The FOM at cycle 600 was 49. These data demonstrate the rapid progress that is being achieved in the development of rechargeable lithium batteries.

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