Stable Dismantling of Spent Lithium Primary Batteries for Recycling

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1. Introduction

The Lithium primary battery that has high energy density and a long life owing to high voltage as 3V, low self-discharge rate and low leakage is used as a backup power source of computer, for watch, calculator, camera, computer game and poise of fishing. The total amount of responsibility about Extended Producer Responsibility was 74 tons in 2004, which is based on an annual out was 255 tons in 2002. The standard recycling cost is 800 thousand won per ton in Korea. The spent Lithium primary battery has been reclaimed to disposal since a recycling technology has not been developed up to now. Recently, it has been known that the china was imported 30 tons of spent Li battery and has recycled it. However we still have no disposal method. The annual sales of VITZROCELL and XENOENERGY, the domestic manufacturer of Li battery, are above 20 billion won and 2 billion won, respectively. And besides ANYCELL produces Li battery, too.

The Lithium primary battery is a general name of battery using lithium metal as the anode active material, a non-aqueous solvent as a electrolyte, and manganese oxide(normal voltage 3V), graphite fluorides(normal voltage 3V), copper oxide(normal voltage 1.55V), thionyl chloride(normal voltage 3.6V) as a cathode active material. The discharge reaction of battery is as the following: on deoxidizing MnO₂ in anode, Li⁺ of a product of electric discharge enter into MnO₂ by diffusion on cathode. The other Li batteries use a complex of (CF)n, SOCl₂, CrO₃, Cu₄O(PO₄)₂, CuO, poly-2-vinyl pyridine Iodine, as anode active material.

<table>
<thead>
<tr>
<th>Anode</th>
<th>Li</th>
<th>LiClO₄</th>
<th>MnO₂ cathode</th>
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<tbody>
<tr>
<td>Total reaction</td>
<td>Li + Mn(IV)O₂ → Mn(III)O₂(Li⁺) (3.5 V), nLi + (CF)ₙ → nC + nLiF (3.1 V)</td>
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<td>8Li + Cu₄O(PO₄)₂ → 4Cu + Li₂O + 2Li₃PO₄ (2.5 V)</td>
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<tr>
<td></td>
<td>4Li + 2SOCl₂ → 4LiCl + S + SO₂ (3.6 V),</td>
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<td></td>
<td>4Li + Cr₃O₈ → Li₄Cr₃O₈ (3.0 V)</td>
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<tr>
<td></td>
<td>2Li + 2SO₂ → 2Li₂S₂O₄ (3.1 V)</td>
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</table>

As Li battery has high energy density, low self-discharge rate. It don’t need to include harmful metals such as Pb, Cd. The amount of consumption used increased in the world market
scale of 700 million, 30 trillion dollars at the 21 century. The development of a single recycling process is difficult because of various components and various electrochemical reactions to be used various purposes. In addition, structures and components of battery exist differently according to the electric discharge rate of battery. So, recycling is difficult. This research focuses on recycling of lithium manganese battery and thionyl chloride lithium battery that used mainly in Korea.

The spent Li battery was reclaimed in ULSAN until 2004. However, recently, our country prohibits from reclamation because a fire broke out during the transportation of the spent Li battery and the explosion occurred repeatedly during the reclamation of the spent Li battery. In this study, we have investigated a safety processing program of the spent Li primary battery by collecting data about the Li primary battery and analyzing property of the spent Li primary battery.

2. Experimental Procedure

The Li battery should be stabilized by electric discharge to recycle the spent lithium primary battery. The process of stable dismantling of spent Li battery is shown in Fig.1. The processes of spent lithium primary battery are composed of Dismantling - Stabilization of lithium - Crushing - Sorting - Magnetic Separation. At the stage of dismantling, the Li battery is separated from a case of battery (ABS resin), electric wires and vinyl are removed from Li battery, and then the Li battery is discharged and stainless case is corroded sectionally using a sulfuric acid aqueous solution. After Li battery stabilized by corrosion and electric discharge is dried for 24 hours and it is crushed. Finally, the crushing products are divided into magnetic and nonmagnetic materials by a magnetic separator.

3. Result and Discussion

32 kg of spent lithium primary generated from army without plastic case was put into sulfuric acid solution of 0.5 M. It was reacted with acid solution. When the inside of spent battery was open by itself, lithium metal in the battery starts to react and turn into the stable material. After this treatment for several days, the spent lithium primary battery was treated stably by crusher without any firing and explosion. Fig.2 shows discharged batteries. We thought that it was caused by stabilization from Li⁺ reaction in the corroded battery.
This result can be analogized to two stages.

1 stage: The outside of Li battery is corroded by an acid solution.

\[ nMe + 2H^+ = Me^{n+} + H_2 \quad (Mc: \text{Metal}) \]

2 stages: The lithium in battery is stabilized.

\[ Li = Li^{n+} + ne^- \]

Discharged batteries  Before and after discharge  Disclosed battery after discharge

Fig.2. Discharged batteries (0.5M H₂SO₄)

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Reference