

### **B-17.3 A Research for Development of the System for Supplying, Running, and Recycling Batteries as Power Sources in Electric Vehicles.**

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#### **Abstract**

Now we are in need to reduce the increasing carbon dioxide (CO<sub>2</sub>) emission by introducing the electric vehicle (EV) which produces no CO<sub>2</sub> while running. In order to promote the mass-introducing of EV, we discussed about (1) the saving of the resources by improvement of the Ni-electrode and (2) the recycling system to supply Pb acid, Ni-Cd, Ni-Fe, and Ni-Zn batteries constantly.

(1) Using  $\alpha$ -Ni hydroxide leads the battery capacity to increase to be 1.6 times as much as  $\beta$ -Ni hydroxide battery. Further, mixing the small amount of Co and Zn hydroxide improved the reversibility in discharge and charge processes. (2) As required resources for EV is smaller than those for other uses except Cd, we have to recover and reproduce the waste of whole the way of use.

**Key Words** Batteries for Electric Vehicle (EV), Recycling System, Saving of Resources, Improvement of Electrode Performance, Reproduction

#### 1. Introduction

Now increasing carbon dioxide (CO<sub>2</sub>) emission leads us to discuss about its influence on the environment on our earth. Emission ratio from vehicle is comparatively high, and about 80 % of emission from transportation class is occupied by vehicle. Because this emission is thought to be enlarged, it is necessary to promote the popularization of the zero emission car with no CO<sub>2</sub> evolution in order to suppress CO<sub>2</sub> emission. From this point of view, it is favorable for us to build up the systems for supplying components of electric vehicles (EV) constantly, especially batteries for power source.

#### 2. Research Objective

Though the battery performance of present limits the type of EV, improvement of the body and battery performance will enable us to introduce many types and a large number of EV. In the case of realization of mass introducing, it is expected that the amount of the materials for battery will multiply. So we are in need to clarify the prospect of supply and demand for battery resources. In this study, we researched the battery resources, improve the battery performance and investigated the possibility of mass introducing, with calculation about amount of required resources from battery performance.

#### 3. Result and Discussion

(1) Research the battery resources

As an object for study, we selected four batteries which could be used practically now, that is, lead acid battery, nickel-cadmium battery, nickel-iron battery, and nickel-zinc battery. With the data of mine resources, recent deposits and outputs of element included in electrodes of these four batteries (Pb, Ni, Cd, Fe and Zn) was investigated. A durable length of time of Pb, Cd and Zn from present deposit base and consumption is shorter than 20 years. From long-term view, batteries other than Ni-Fe has more or less problem of mineral resources (Table 1).

(2) To improve the battery performance

Since lead acid battery has been well developed, we have studied to improve the performance of nickel hydroxide electrode widely used in various kinds of Ni-batteries, e.g. Ni-Cd, Ni-Fe and Ni-Zn batteries.

At first, the crystal structure and properties of the nickel hydroxides were characterized at the oxidized and reduced state. The results obtained for  $\alpha$ -Ni(OH)<sub>2</sub> in 1M KOH solution are: (a) it leaves electrons 1.6 times more than  $\alpha$ -form, and has higher redox potential than  $\beta$ -form by ca. 50 mV, (b) so-called " $\gamma$ -NiOOH" at oxidized state is not an oxyhydroxide but an oxide, and water is intercalated between NiO<sub>2</sub> layers (Table 2), (c) charge/discharge reversibility is better than  $\beta$ -form for film thickness between 10 and 10000 nm, (d) it also shows a better long term stability for more than 400 cycles in spite of large expansion/relaxation in crystal lattice upon the redox reaction. The problem of  $\alpha$ -Ni(OH)<sub>2</sub> is the chemical instability, because it is easily transferred to  $\beta$ -form.

It was verified for metal hydroxides, i.e., Ni<sub>x</sub>Co<sub>y</sub>Zn<sub>z</sub>(OH)<sub>2</sub>, here x, y and z can be controlled, prepared by cathodic deposition from mixed nitrate solutions that: (a) the crystals have the  $\alpha$ -form structure, (b) contrast with the pure  $\alpha$ -Ni(OH)<sub>2</sub>, the crystals are quite stable and never transferred to  $\beta$ -form, (c) charge/discharge characteristics of the materials are much improved due to the catalytic properties of cobalt and zinc (Table 3).

In conclusion, the nickel resources will be more efficiently utilized, if  $\alpha$ -Ni(OH)<sub>2</sub> and/or solid solution of Ni<sub>x</sub>Co<sub>y</sub>Zn<sub>z</sub>(OH)<sub>2</sub> are used as electrode materials of the Ni-batteries instead of  $\beta$ -Ni(OH)<sub>2</sub>.

(3) Amount of required resources at mass introducing EV

we calculate an amount of required resource for battery during 10 years after mass introducing realization, with setting the parameters of number of EV, recycling ratio of battery, energy density (power density) of battery, and so on. Generally, required amount is calculate with a basis of battery capacity, but in driving practically, people pay attention to a speed of car which has close relation to power of battery. From this reason, we took a method of calculating with power of car and power density of battery.

First, we tried to calculate required amount with a basis of battery capacity, from present specifications of prototype or production vehicles (van type). When ten thousands of EVs are introduced, required quantities are thought to be : about 1600 t of Pb in lead acid battery, 50 t of Ni and 75 t of Cd in Ni-Cd battery, 70 t of Ni and 70 t of Fe in Ni-Fe battery, and 50 t of Ni and 85 t of Zn in Ni-Zn battery.

Next, we calculated similarly with a basis of power density of battery. At the same time, we examined an amount of resources by comparing the required quantity and the deposit base of every element. As a 1st case, following conditions were set : recycling ratio of battery is one-third, that of material used other than battery is zero : if energy density of lead acid, Ni-Cd, Ni-Fe, and Ni-Zn battery is 40, 50, 60, 70 Wh/kg respectively, they can be used 40, 45,

40, 50 W/kg in power density, respectively. As a result, after ten years, 90 % of deposit base for Fe and Ni, 70 % for Cd and Zn, 50 % for Pb will have remained. In the case of Pb, thinking only about use for battery, 97 % will have remained. If a large number of EV loading lead acid battery are introduced, it is afraid that lead resources will exhausted.

If the number of introduced EV increases to be 100 thousand (Fig. 1) or million (Fig. 2) in this system, much resources are recycled and there will be no problem of resources in the case except for Cd.

We have several point of improvement required in this way of calculation. Moreover we cannot get enough data for battery performance in practical use on road. But from these result, it is revealed that, in the case of mass introducing of EV, not only the battery performance improvement but also the consolidation of social system is indispensable to supply a lot of battery constantly where a large part of resources is recycled.

As a basis of these results, we will investigate a method for recovery and reproduction of battery and design the social systems for establishment of recycling system. We will also try to decrease a resources by improvement of battery utilization.

Table 1 Data of mine resources

	deposit (million ton)	output at 1988 (million ton)	consumption (year)
Pb	140	5.72	19
Ni	100	0.85	48
Cd	0.97	0.022	27
Fe	89,000	918	126
Zn	300	7.25	19

Table 2 Frequency shift of  $\nu(\text{Ni-O-H})$  band according to deuterium substitution

	$\alpha\text{-Ni(OH)}_2$		$\beta\text{-Ni(OH)}_2$		$\gamma\text{-NiOOH}$		$\beta\text{-NiOOH}$	
	H	D*	H	D*	H	D*	H	D*
IR	647	636	550	534	578	578	571	559
Raman	475	425	450	439	475	474	479	464

D\*: compounds substituted with deuterium.

Table 3 Redox electricity and coulomb efficiency of metal hydroxides

composition	cycles	Oxidation $e^-/Ni^*$	Reduction $e^-/Ni^*$	Efficiency (%)
$\alpha-Ni(OH)_2$	1	1.6	1.1	74
	357	0.70	0.50	70
$\alpha-Ni_{0.5}Co_{0.5}(OH)_2$	1	1.8	1.6	90
	350	1.1	0.98	91
$\alpha-Ni_{0.5}Zn_{0.5}(OH)_2$	1	0.40	0.40	100
	340	0.40	0.40	91
$\alpha-Ni_{0.3}Co_{0.2}Zn_{0.5}(OH)_2$	1	0.61	0.52	85
	400	0.62	0.62	100

$e^-/Ni^*$ : electron/Ni atom

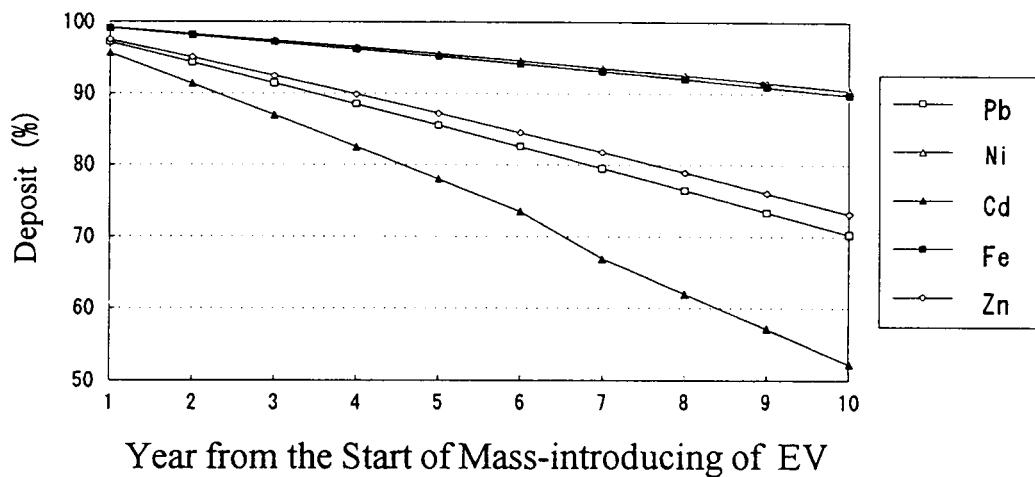


Figure 1 Calculated value of remained deposit after introducing 100 thousand EVs per year.

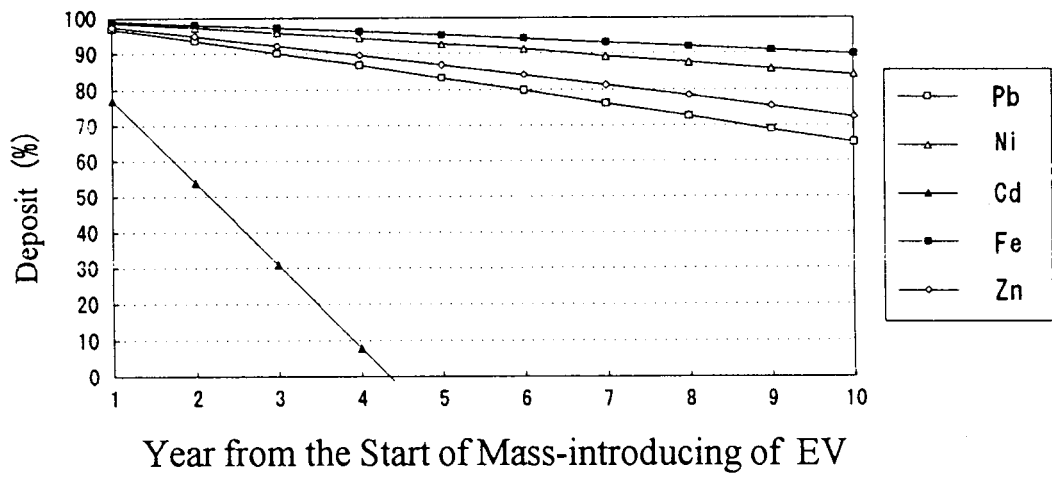


Figure 2 Calculated value of remained deposit after introducing a million EVs per year.