EFFECT OF THE LITHIUM EXCESS ON PERFORMANCE OF LiCoO₂

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Introduction

This article is aimed on preparing and measuring the positive electrode base on $LiCoO_2$ with and without the excess of lithium. It's well known that the excess of lithium during the preparation increase an electrical conductivity of the material [1]. Thus, the material with the excess of lithium should show better characteristics then the material without the excess [2].

The increasing demand for portable and cordless electronic devices is urging the development of compact and small batteries. Especially, lithium ion batteries have attracted much attention because of the high output voltage, high specific energy and long lifecycle. Lithium transition metal oxides, such as $LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$, have been investigated in order to apply them as positive electrode materials for lithium secondary batteries. Research on $LiCoO_2$ has been more active because this material is the most promising in spite of its high cost and toxicity.

Experimental

LiCoO₂ materials were prepared from LiNO₃ (purity 99 %) and Co (NO₃)₂ .6H₂O (purity 99 %). These materials were accurately weighted and mixed together with molar ratio of Li: Co=1:1 (1.1:1 and 1.2:1 with lithium excess) in the mortar. The mixtures were dried at 90 °C and 120 °C for 2 h and 4 h in the air. Then the mixtures were crushed in the mortar. Afterwards the mixtures were annealed at 400 °C for 2 h, at 600 °C for 2 h and at 800 °C for 6 h in the air. The final products were pulverized in the mortar.

The positive electrode material was prepared by mixing the $LiCoO_2$ powder, carbon black, expanded graphite and teflon at weight ratio of 85:5:5:5. A small amount of ethanol was added to the mixture for making the proper paste. The resultant paste was coated on the nickel mesh. The coated mesh was pressed and dried at 150 °C for 1 h. The positive electrode was prepared.

Two electrode cell was assembled to examine galvanostatic discharge behaviors. A piece of lithium metal (purity 99.9 %) was used as a counter and reference electrode. The working (positive) electrode is described above. 1 M LiClO₄ (purity 95 %) in EC-DEC (purity 99 %) was used as electrolyte. The working electrode was charged at a constant voltage of 4.2 V for 2 h. Afterwards this electrode was discharged to 3 V (vs.Li) at a constant current of 70 mA/g. Three cycles were measured for the each sample. The AUTOLAB PGSTAT 30 was used for the measurement.

Results and Discussion

The results are shown in the tables 1 and 2. The results correspond to the theoretical presumption [3]. $LiCoO_2$ with the excess of lithium shows a higher specific capacity. All samples shows Columbic efficiency around 80%.

 Table 1
 LiCoO2 with the excess of lithium (20 %)

Number	Obtained capacity	Q-/Q+	Specific capacity			
of scan	(3-4.2 V)					
	[%]	[%]	C/g			
1	45	78	384			
2	43	85	366			
3	40	85	342			

 Table 2
 Comparison of materials

Number	LiCoO ₂	Li _{1.1} CoO ₂	$Li_{1.2}CoO_2$
of scan			
	C/g	C/g	C/g
1	354	382	384
2	336	367	366
3	314	339	342

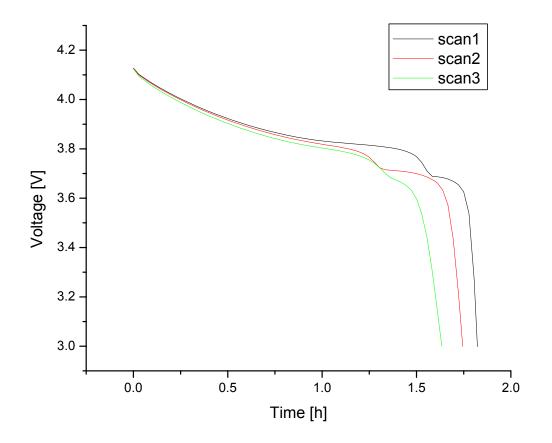


Fig. 1 Discharge characteristics of LiCoO₂ with the excess of lithium (20 %)

Conclusion

The results show that $LiCoO_2$ with the excess of lithium exhibits a higher specific capacity then $LiCoO_2$.

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References

- Carewska, M., Scaccia S.: Electrical conductivity and Li NMR studies of Li1+yCoO2, Solid state ionics 93 (1997) 227-237
- [2] Choi.H.S., Shlyakhtin O.A: Structural and electrochemical properties of Li 1+xNi 0.5Mn 0.5O 2+δ (0 ≤ x ≤ 0.7) cathode materials for lithium-ion batteries, Journal of Power Sources 140(2005) 355-360
- [3] Pistoia, G.: Lithium batteries. New materials, developments and perspectives, Industrial, Chemistry Library, The Netherlands 1994