

The Electrochemical Properties of Nano-Sized Cobalt Powder as an Anode Material for Lithium Batteries

Dong-Yeon Kim,¹ Hyo-Jun Ahn,^{1,*} Jong-Seon Kim,¹ Ic-Pyo Kim,¹ Jeong-Hui Kweon,¹
Tae-Hyun Nam,¹ Ki-Won Kim,¹ Jou-Hyeon Ahn,² and Seong-Hyeon Hong³

¹School of Materials Science and Engineering, ReCAPT, Gyeongsang National University, Jinju, 660-701, Korea

²Department of Chemical & Biological Engineering, Gyeongsang National University, Jinju, 660-701, Korea

³Powder Materials Center, Korea Institute of Machinery and Materials, Changwon, 641-830, Korea

The nano-sized cobalt powders were prepared using a pulsed wire evaporation method. The cobalt powder had a spherical shape with a diameter of less than 200 nm. A cobalt electrode was prepared from the nano-sized cobalt powder, acetylene black and polyvinylidene fluoride. During the first discharge, the Li/Co cell showed a plateau potential of 0.7V and a capacity of 440mAh/g. The nano-sized Co electrode had a stable reversible lithium storage capacity of approximately 280mAh g⁻¹ after 30 cycles.

Keywords: Nano-sized cobalt powder, electrochemical property, anode, Li-ion battery

1. INTRODUCTION

Lithium ion batteries are popular power sources for cellular phones, notebook computers, and hybrid electric vehicles (HEVs). Lithium ion batteries are composed of a graphite anode and lithium transition metal oxides such as LiCoO₂, LiNiO₂, and LiFePO₄. A considerable amount of effort has been made to develop new anode materials to replace the graphite currently used in these batteries, which has a low theoretical capacity of 372 mAh g⁻¹.^[1-3]

There are many candidates with different forms for this new anode material, including different elements,^[4,5] inter-metallic compounds,^[6,7] active/inactive nano-composites,^[8,9] and thin film materials.^[10-13] Among the potential candidates for use as an anode material are cobalt composites such as Co-O,^[14] Co-Sn,^[15] Co-C,^[16] and Co-Sb.^[17] As nano-sized powders show good electrochemical performance, numerous studies have been conducted on the subject of electrodes using nano-sized materials. However, no reports exist regarding the electrochemical properties of an electrode that uses nano-sized cobalt powder. Nano-sized powder can be prepared by a range of methods, including sol-gel,^[18] solvothermal,^[19] spray conversion^[20] and pulsed wire evaporation (PWE) methods.^[21] In particular, the pulsed wire evaporation method can be used to fabricate nano-sized particles with a homogeneous quality and a high yield.

In this work, a cobalt electrode was prepared using nano-sized cobalt powders and the electrochemical properties of

the cobalt electrode prepared as an anode material for lithium batteries was investigated.

2. EXPERIMENTS

The nano-sized cobalt powders were fabricated by a pulsed wire evaporation method. The cobalt electrode was composed of 70 wt.% nano-sized Co powder, 20 wt.% acetylene black carbon (Aldrich) and 10 wt.% copolymer of polyvinylidene fluoride-co-hexafluoropropylene (PVdF-co-HFP; Kynar 2801, Atochem). Cobalt, PVdF-co-HFP and carbon in 1-methyl-2-pyrrolidone (NMP) were mixed homogeneously using a planetary ball mill for 3h and were then pasted onto Cu foil. The cobalt electrodes thus manufactured were then dried in a vacuum chamber for 48 h. The electrolyte was 1M LiPF₆ dissolved in a 1:1 (w/w) mixture of ethylene carbonate (EC) and dimethylene carbonate (DMC). The cell was stacked with a lithium disk, electrolyte and a cobalt electrode in turn in a glove box filled with argon. Electrochemical tests were carried out between 0.01 and 3.0 V at room temperature. The surface morphologies and shape of the particles were observed with a scanning electron microscope (SEM, JEOL-5600) and a transmission electron microscope (TEM, JEM-2010), respectively. X-ray diffraction (XRD) patterns were collected using a Bruker diffractometer D8 with Cu K α radiation ($\lambda=1.5406$).

3. RESULTS AND DISCUSSION

SEM images of the raw materials (Co, C and PVdF-co-

*Corresponding author: ahj@gnu.ac.kr

HFP) are shown in Fig. 1. Cobalt powders exhibited spherical nano-sized particles with a diameter of less than 200nm. The PVdF-co-HFP powder showed a homogeneous spherical shape and the carbon powder showed a cluster agglomerated by particles with sub-micrometer diameters. Figure 2 presents the X-ray diffraction patterns of the raw materials. The nano-sized cobalt powder had a face-centered cubic (FCC) structure. Cobalt has a hexagonal structure at room temperature; however, it has an FCC structure at temperatures that exceed 422°C. Thus, nano-sized cobalt powder has a high temperature phase, which may be related to the PWE fabrication method. The broad peak of the PVdF-co-HFP and the carbon can be explained by the amorphous structure.

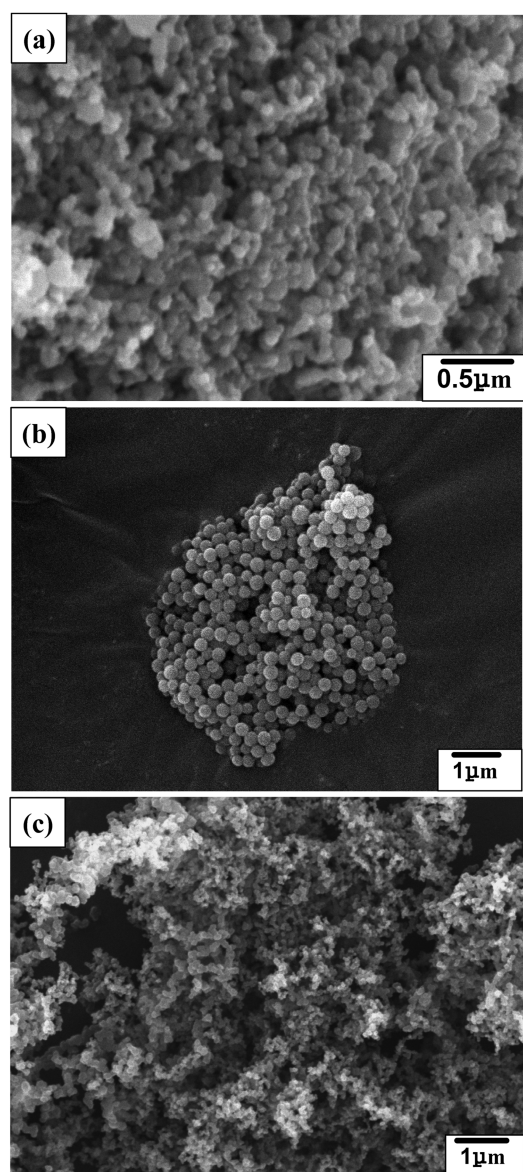


Fig. 1. SEM morphologies of raw materials for cobalt electrode: (a) cobalt powder, (b) PVdF-co-HFP, and (c) carbon.

Figure 3 shows the first discharge curves of a Li/Co cell between 0.01 and 3.00 V at a constant current density of 100mA g^{-1} . The discharge curve showed a plateau potential at 0.7V. The first discharge capacity was 440mAh g^{-1} , which can be matched to 1.8 Li per Co. Given that this is the first report of a nano-sized cobalt powder, the data was compared with that from a thin film cobalt electrode fabricated by PLD (Pulsed Laser Deposition).^[11] The cobalt thin film had both a cubic and a hexagonal structure. The cobalt film electrode showed sloping behavior without a plateau region with a first discharge capacity of nearly 290mAh/g . This is less than that of the cobalt nanopowder used in this experiment. The difference may derive from the thin film shape and crystal structure.

Figure 4 shows the changes in the SEM images of the cobalt electrode after a discharge. The original cobalt electrode had a homogenous mixture and rough surface morphology. After a discharge, the surface of the cobalt electrode

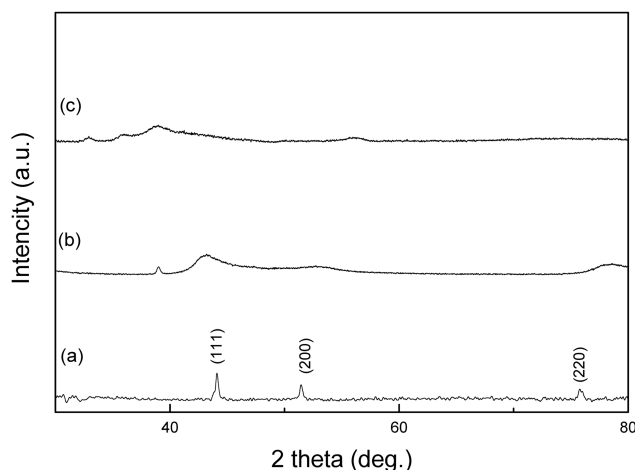


Fig. 2. XRD patterns of raw materials for cobalt electrode: (a) cobalt powder, (b) carbon, and (c) PVdF-co-HFP.

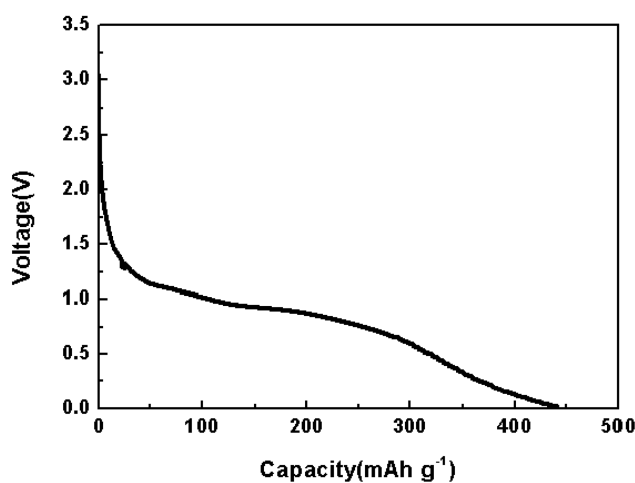


Fig. 3. The first discharge curves of a Li/Co cell.

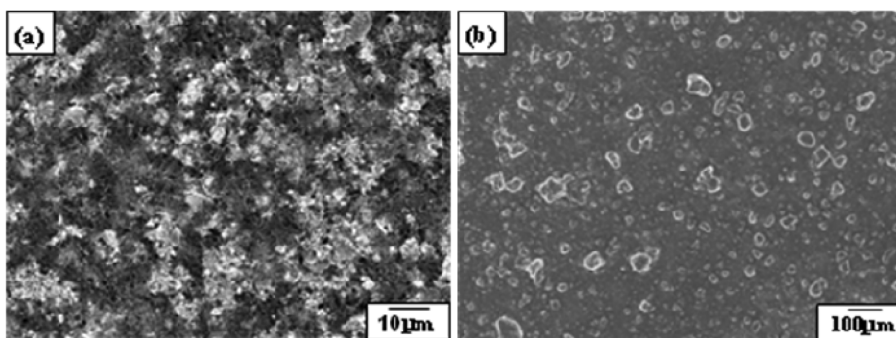


Fig. 4. The SEM morphologies of cobalt electrode: (a) before discharge and (b) after first discharge.

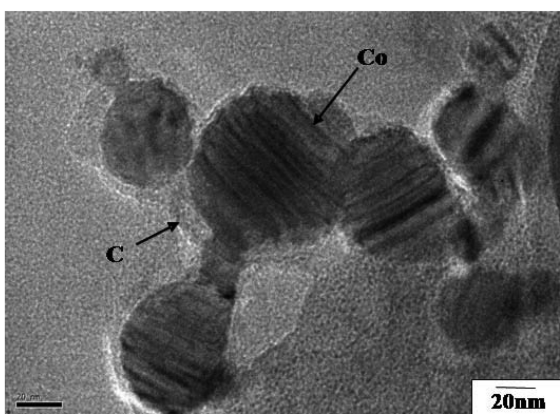


Fig. 5. The TEM micrographs of cobalt electrode after first discharge test.

was covered with a film.

Figure 5 shows TEM micrographs of the cobalt electrode after the first discharge test. The cobalt powder had a spherical shape with a diameter of approximately 50 nm. These particles show regular lattice directions. Moreover, all cobalt particles are fully coated with a smooth and uniform layer. There have been many reports that found that carbon could be coated onto an oxide electrode by ball milling.^[22] As the cobalt electrode was prepared through 3hrs of ball milling, the surface of the cobalt powder may be covered by carbon.

Figure 6 shows the discharge/charge profiles of the 1st, 2nd, 15th and 30th cycle. A large irreversible capacity was observed in the 2nd cycle, which was similar to that observed in the cobalt thin film.^[11] The discharge capacity decreased to 240 mAh g⁻¹ after 30 cycles. The cyclic performance is shown in Fig. 7. This figure shows that 70% of the reversible capacity could be maintained during 20 cycles at a current density of 100 mA g⁻¹.

The electrochemical properties of nano-sized cobalt have not been reported. Moreover, cobalt is considered as an inert material and not as an anode material. However, the nano-sized cobalt showed good electrochemical properties in this experiment; this may be related to its nano-sized diameter

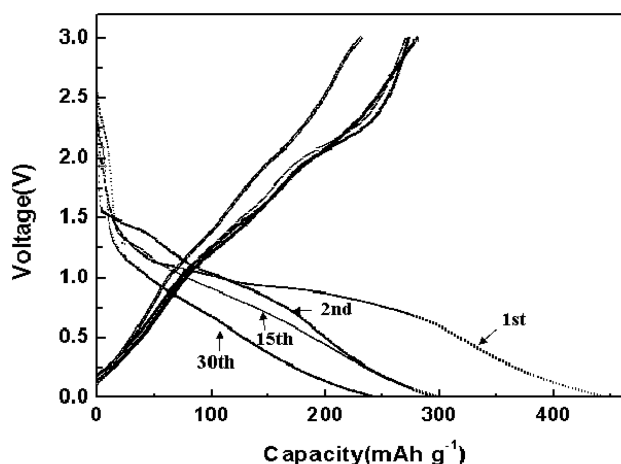


Fig. 6. The discharge/charge profiles of 1st, 2nd, 15th and 30th cycles.

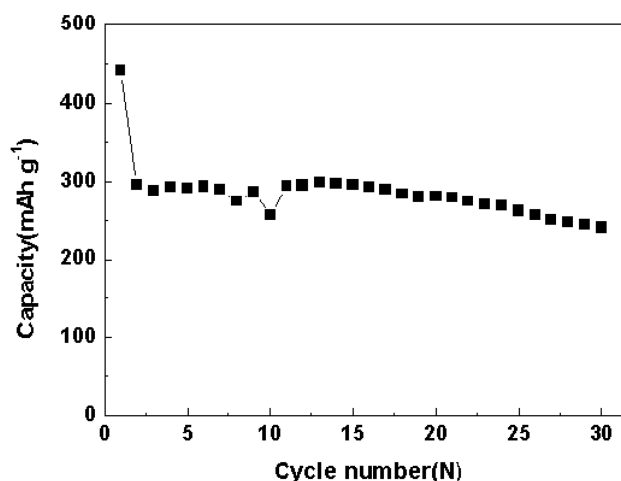


Fig. 7. The change of capacity with repeated cycling for Li/Co cell.

and the high temperature phase of its FCC structure. The reversible capacity may be due to a reaction in which the lithium intercalated into the cobalt phase to form Li-Co alloy phases. However, the Li-Co reaction mechanism was not clearly defined. Hence, further research is needed in this area.

4. CONCLUSIONS

Nano-crystalline cobalt electrodes were fabricated with a homogeneous distribution of raw materials by a ball-milling process. The first discharge curve of the Li/Co cell showed a plateau potential of 0.7V and a capacity of 440mAh/g. The nano-sized cobalt electrode had a stable reversible lithium storage capacity of approximately 280mAh g⁻¹ after 30 cycles. The first discharge capacity of the cobalt electrode was higher than that of the graphite anodes used in current lithium ion batteries; however, the cycle property was poor. In addition, the nano-sized cobalt powder exhibited electrochemical characteristics that differed from those of conventional cobalt powders.

ACKNOWLEDGEMENTS

This work was supported by Pioneer Research Center for Nano-morphic Biological Energy Conversion and Storage.

REFERENCES

1. Y. Wang and J. Y. Lee, *J. Phys. Chem. B* **108**, 17832 (2004).
2. N. Perira, L. Dupont, J. M. Trascon, L. C. Klein, G. G. Amatucci, *J. Electrochem. Soc.* **150** (2003).
3. L. J. Fu, H. Liu, Y. P. Wu, E. Rahm, R. Holze, and H. Q. Wu, *Prog. Mater. Sci.* **50**, 881 (2005).
4. I. Rom, M. Wachtler, I. Papst, M. Schmied, J.O. Besenhard, F. Hofer, and M. Winter, *Solid State Ionics* **143**, 329 (1999).
5. M. M. Thackeray, J. T. Vaughan, C. S. Johnson, A. J. Kropf, R. Benedek, L. M. L. Fransson, and E. Edstron, *J. Power Sources* **113**, 124 (2003).
6. Y. U. Kim, C. K. Lee, H. J. Sohn, and T. Kanga, *J. Electrochem. Soc.* **151**, A933 (2004).
7. J. Xie, G. S. Cao, X. B. Zhao, Y. D. Zhong, and M. J. Zhao, *J. Electrochem. Soc.* **151**, A1905 (2004).
8. D. G. Kim, H. Kim, H. J. Sohn, and T. Kang, *J. Power Source* **104**, 221 (2002).
9. J. Wolfenstine, S. Campos, D. Foster, J. Read, and W. K. Behl, *J. Power Sources* **109**, 230 (2002).
10. H. Mukaibo, T. Sumi, T. Yokoshima, T. Momma, and T. Osaka, *Electrochem. Solid-State Lett.* **6**, A218 (2003).
11. V. Pralong, J. B. Leriche, B. Beaudoin, E. Naudin, M. Morcrette, and J. M. Tarascon, *Solid State Ionics* **166**, 295 (2004).
12. B. S. Jeon and S. M. Lee, *Electron. Mater. Lett.* **5**, 13 (2009).
13. M. K. Jung, S. M. Park, D. W. Park, and S. R. Lee, *J. Kor. Inst. Met. & Mater.* **47**, 378 (2009).
14. Y. Liu, C. Mi, L. Su, and X. Zhang, *Electrochimica Acta* **53**, 2507 (2008).
15. Y. Zheng, J. Yang, Y. Nuli, and J. Wang, *J. Power Sources* **174**, 624 (2007).
16. G. F. Ortiz, R. Alcántara, I. Rodríguez, and J. L. Tirado, *J. Electroanal. Chem.* **605**, 98 (2007).
17. J. Xie, X. Zhao, G. Cao, Y. Zhong, and M. Zhao, *J. Electroanal. Chem.* **542**, 1 (2003).
18. Y. S. Lee, Y. K. Sun, and K. S. Nahm, *Solid State Ionics* **118**, 159 (1999).
19. J. Xie, X. B. Zhao, G. S. Cao, Y. D. Zhong, M. J. Zhao, and J. P. Tu, *Electrochim. Acta* **50**, 1903 (2005).
20. S. H. Hong, J. S. Bae, and H. J. Ahn, *Met. Mater. Int.* **14**, 229 (2008).
21. Y. R. Uhm, J. H. Park, W. W. Kim, C. H. Cho, and C. K. Rhee, *Mater. Sci. Eng. B* **106**, 224 (2004).
22. J. K. Kim, G. Cheruvally, J. H. Ahn, and H. J. Ahn, *J. Phys. Chem. Solids* **69**, 1257 (2008).