

Short communication

Fabrication and characterization of a LiCoO₂ battery–supercapacitor combination for a high-pulse power system

Sun Hee Choi^a, Joosun Kim^a, Young Soo Yoon^{b,*}

^a Nano-Materials Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, South Korea

^b Department of Advanced Fusion Technology, Center for Emerging Wireless Power Transmission Technology, Konkuk University, Seoul 143-701, South Korea

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Abstract

The performance of portable electronic equipment can often be improved by including an electrochemical capacitor alongside the battery. The capacitor extends battery life by reducing its peak output power. A CR2032 coin-type battery cell was used for the LiCoO₂ cathode and Li anode. A mixture of 1 M LiPF₆-ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 vol, Merk) was used as the electrolyte.

The electrochemical characteristics of a supercapacitor are able to provide a much higher pulse current capability than the battery system. By combining a supercapacitor and a battery, the pulse performance of a battery can be significantly improved according to various pulse times.

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1. Introduction

Recently, lithium-ion batteries have been applied in a wide range of uses including portable computers and mobile telephones just to name a few. Phone batteries must be able to supply repetitive high-current pulses, perhaps up to a 10C discharge rate. This can severely stress many of the battery systems, particularly during operation at low temperatures. While batteries store a lot of energy and release the stored charge stably, supercapacitors deliver a high current, but only for a very short time. That is, although supercapacitors release their peak current when the devices begin operation, batteries give off a stable current while in use. The performance of portable electronic equipment can often be improved by including a supercapacitor alongside the battery. The capacitor extends a battery's life by reducing its peak output power. A supercapacitor can provide high power density as well as sufficient energy density. A

Ragone plot is shown in Fig. 1. Clearly, the supercapacitor offers the best combination of power and energy density. Furthermore, by combining the best features of the battery and the supercapacitor, a superior system may result.

At a high discharge rate, such as the pulse current, the heat generated inside a battery is significant. This not only reduces the efficiency of the electrical energy generation, but also causes deleterious effects (i.e. shortened cycle life and increased internal resistance). With an electrochemical capacitor, it would be expected that only a minimal heat is generated from I^2R . Clearly, electrochemical capacitors should possess a high efficiency even at a rapid rate of discharge. Therefore, for pulse power applications, the electrochemical capacitor should help the battery to deliver higher power in a more efficient manner [1].

In this experiment, we used a LiCoO₂ battery–supercapacitor combination. LiCoO₂, heat-treated above 700 °C (HT-LiCoO₂), has a high cycle life compared to other cathode materials, such as LiNiO₂ and LiMn₂O₄. The lattice is formed by oxygen atoms in ABC stacking with alternating

* Corresponding author. Tel.: +82 2 2049 6042; fax: +82 2 452 5558.

E-mail address: ysyoon@konkuk.ac.kr (Y.S. Yoon).

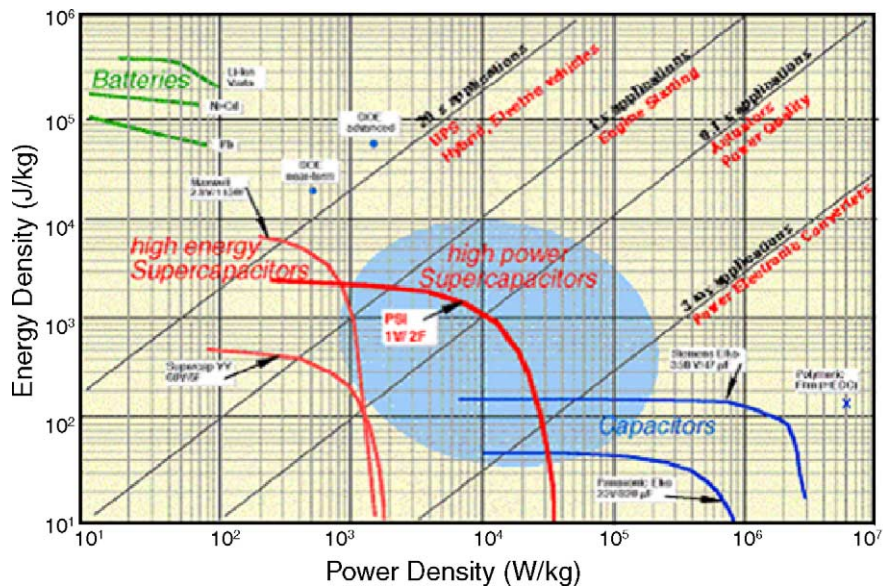


Fig. 1. Ragone plot for energy systems.

layers of Li and Co ions in octahedral interstitial sites between the oxygen planes [2–5]. The combination of salt encapsulation with an earlier proposed powder engineering technique [6,7] ensures fine particle size control of LiCoO₂ powders obtained using wet chemical methods [8].

2. Details of experiment

An aqueous solution of Li and Co acetates (Li/Co = 1.1) was frozen by spraying on liquid nitrogen followed by freeze-drying for two days at $P = 5 \times 10^{-2}$ mbar (Alpha 2-4, Christ). A part of the freeze-dried product was mixed with K₂SO₄ (1:10) and subjected to planetary milling (Pulverisette-5, Fritsch) in ZrO₂ media at 600 rpm for 24 h (ball to powder mass ratio 10:1). Thermal decomposition of a precursor and of a precursor mixture with K₂SO₄ was performed in air first at 400 °C for 10 h, then at 800 °C for 12 h. The thermally processed mixture was washed with distilled water several times in order to eliminate SO₄²⁻ ions; LiCoO₂ residue was then separated by centrifugation. Obtained LiCoO₂ powders have been studied by XRD (Geigerflex, Rigaku, 2°/min, Cu Kα), scanning electron microscopy (SEM, Philips ESEM), and TEM (Philips CM-30, $U = 200$ kV). Commercial LiCoO₂ powder, supplied by Seimi Co., was used for comparison.

Electrochemical characterizations were performed using a CR2032 coin-type cell with the following parameters: cut-off voltage 3.2–4.2 V and $I = 0.5$ mA (pulse current: 5 mA, 1 s) at room temperature. The pulse circuit was tested using two different configurations: a battery only configuration and a battery/supercapacitor configuration, which is a battery in parallel with the supercapacitor. Commercial supercapacitors supplied by Samsung Co. were used.

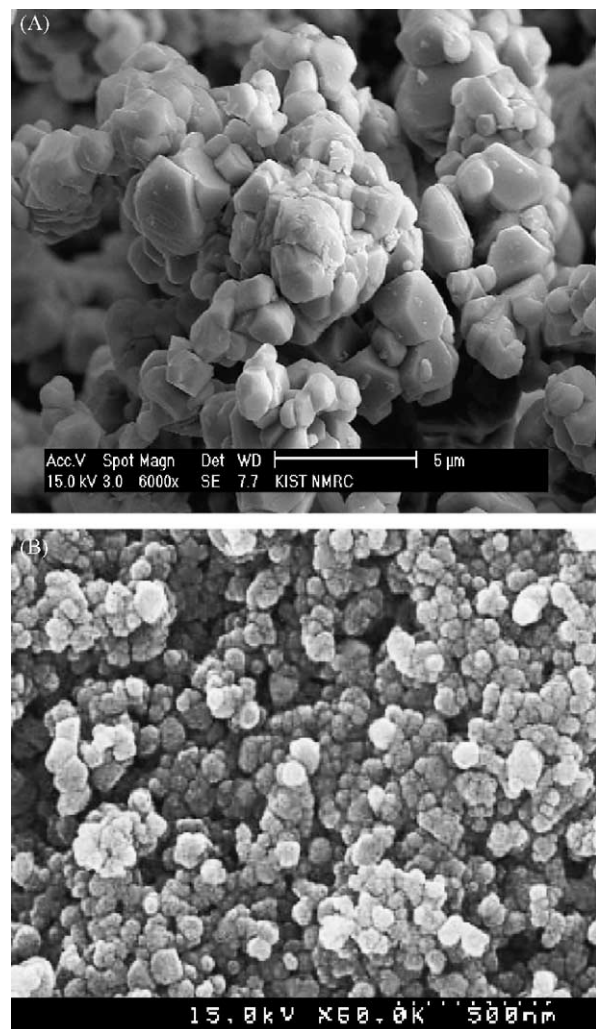


Fig. 2. SEM micrographs of LiCoO₂ powders (A) Seimi Co. and (B) planetary processing with K₂SO₄.

The cathode was fabricated with 20 mg of accurately weighed active material and 12 mg of conductive binder (8 mg of teflonized acetylene black (TAB) and 4 mg graphite). The cathode was pressed on 200 mm² stainless steel mesh, which was used as the current collector, under a pressure of 300 kg/cm² and subsequently dried at 180 °C for 24 h in a vacuum oven. The test cell was made of cathode and a lithium metal as an anode separated by a porous polypropylene film (Celgard 3401). A mixture of 1 M LiPF₆-ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 vol, Merk) was used as the electrolyte.

3. Results and discussion

SEM analysis of the LiCoO₂ powders, obtained by matrix isolation of precursor particles by K₂SO₄, confirmed the efficiency of this method in terms of grain coarsening prevention. Commercial Seimi Co. powder (powder A) formed micron-sized crystallites (Fig. 2 A), while K₂SO₄-processed powder (powder B) was characterized by a grain size distribution in a range of 30–70 nm (Fig. 2B).

XRD analysis of micron-sized (powder A) and nanocrystalline powders (powder B) revealed the formation of single phase hexagonal HT-LiCoO₂ in both cases (Fig. 3). Process-

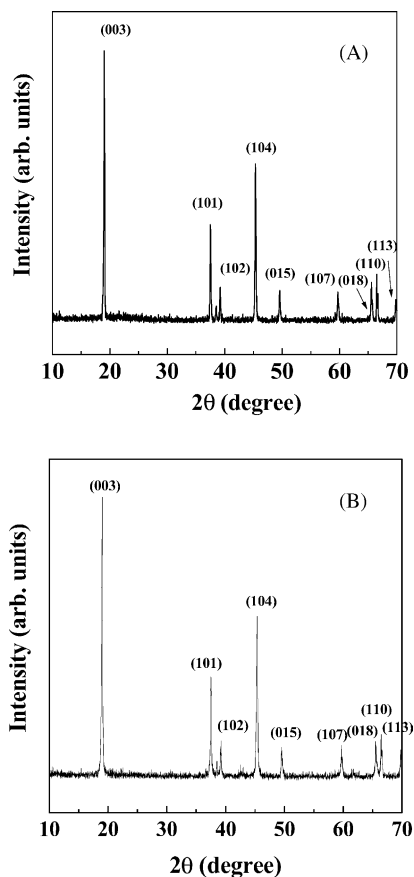


Fig. 3. XRD patterns of (A) coarse-grained Seimi Co. and (B) nanocrystalline LiCoO₂ powders.

ing of LiCoO₂ powders at 800 °C in contact with K₂SO₄ was not accompanied by formation of secondary phases or by significant displacement of the main reflections displayed in the formation of solid solutions. Sharp and well-resolved reflections of both patterns were observed at perfect crystallographic ordering. The uncharacteristic (003)/(104) peak ratio for the nanocrystalline powder can be related to anomalies of element distribution within the Co sublattice [9].

Fig. 4 shows the first cycle charge and discharge behavior for (A) LiCoO₂ battery (B), the coarse-grained LiCoO₂ battery with pulse current (C), and a nanocrystalline LiCoO₂ battery with pulse current. In Fig. 4(B) and (C), the charge current is 0.5 mA/cm² and the pulse discharge current is a repetition of 0.5 mA/cm² for 10 s (*t*₁) and 5 mA/cm² for 1 s (*t*₂). In Fig. 4(A), the smaller discharge capacity of the nanocrystalline LiCoO₂ battery is due to the partial cubic spinel phase in nanocrystalline powder [10]. However,

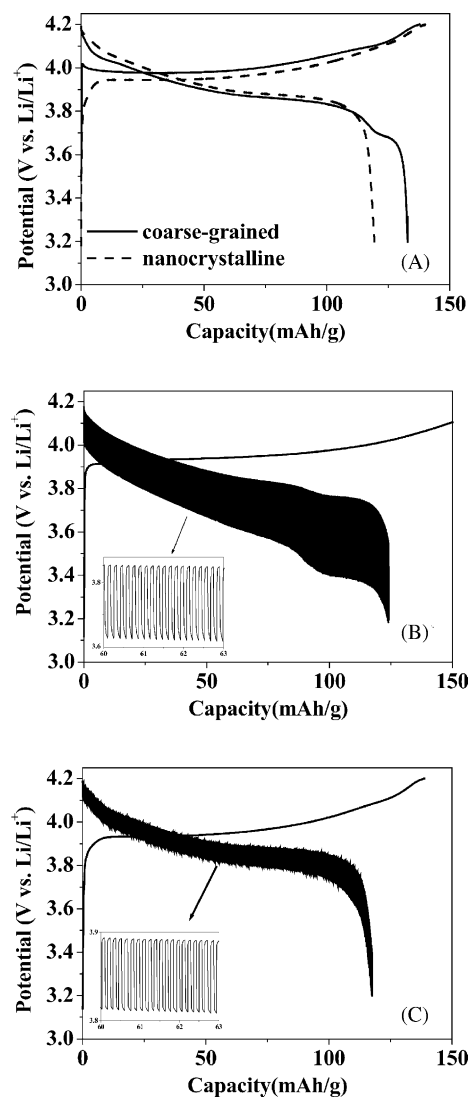


Fig. 4. First cycle charge and discharge behavior for (A) LiCoO₂ battery, (B) coarse-grained LiCoO₂ battery with pulse current and (C) nanocrystalline LiCoO₂ battery with pulse current.

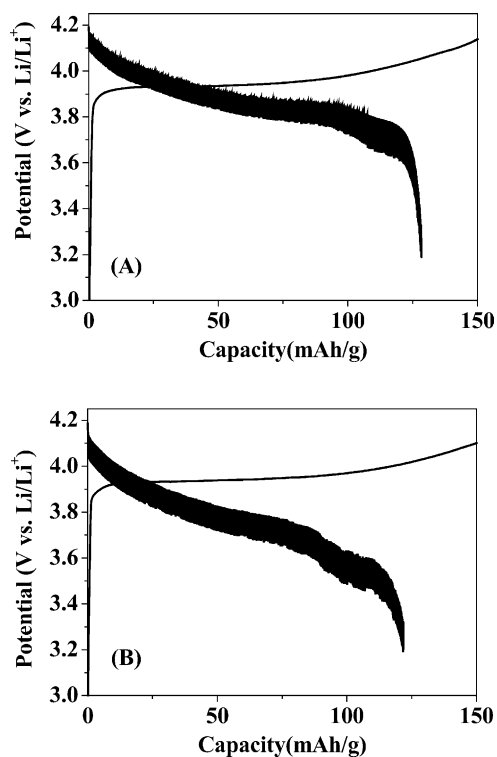


Fig. 5. First cycle charge and discharge behavior for coarse-grained LiCoO_2 battery–supercapacitor combination with pulse current (A) $t_1 = 10$ s and (B) $t_2 = 2$ s.

comparison of Fig. 4(B) and (C), suggests the better pulse performance of nanocrystalline powder can be attributed to the smaller particle size. This smaller particle size ensures a shorter mean length of Li diffusion pathways from its position in the LiCoO_2 lattice to the cathode–electrolyte interface. In addition, diffusion through the grain boundary of nanocrystalline powder is larger than that of the coarse-grained powder. Shorter diffusion distances promote faster and uniform Li intercalation into LiCoO_2 crystallites during the discharge process compared to coarse-grained powder, thus improving high-pulse performance.

Fig. 5 shows the first cycle charge and discharge behavior for coarse-grained LiCoO_2 battery–supercapacitor (0.47F) combination (A) $t_1 = 10$ s and (B) $t_1 = 2$ s. In the case of coarse-grained powder, pulse performance is greatly improved owing to the combination with an electrochemical capacitor when compared to Fig. 4(B). We confirmed that the pulse performance of the battery could be significantly improved by combining a supercapacitor and a battery. When the amount of time of low discharge current is short

(Fig. 5(B)), the cell shows poorer pulse performance compared to Fig. 5(A). In order to improve pulse performance, enough time to recover the cell is needed. Although a certain amount of time is required, pulse performance is improved due to its combination with an electrochemical capacitor.

4. Conclusion

The electrochemical characteristics of the supercapacitor can provide a much higher pulse current capability than a battery system. By combining a supercapacitor with a battery, the pulse performance can be significantly improved for various pulse times. The better pulse performance of nanocrystalline powder is due to the smaller particle size. Shorter diffusion distances promote faster and uniform Li intercalation into LiCoO_2 crystallites during the discharge process compared to that of coarse-grained powder, thus improving pulse performance. Although sufficient time is needed, high-pulse performance is improved due to combination with an electrochemical capacitor.

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