$LiCoO_2$ SYNTHESIZED BY A TEA-SUCROSE COMBUSTION METHOD AS A CATHODE MATERIAL IN LITHIUM BATTERIES

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Since the serendipitous synthesis of α–alumina by rapid heating of aluminum nitrate-urea solutions [1], much interest has developed in solution-based combustion synthesis of oxidic materials. This method provides several advantages: simple and economic preparation, easy control of homogeneity and stoichiometry, easy incorporation of dopants/substituents, and production of fine-particulate, high surface area materials. The electrochemical behavior of $LiCoO_2$ synthesized with triethanolamine (TEA) and sucrose as fuels, and nitrates of cobalt and lithium as oxidants is presented here. The synthesis involves the molecular dispersion of the nitrates in a polymeric matrix of TEA and sucrose, followed by deflagration to the oxidic product in a carbonaceous substrate. Subsequent calcination at 800°C for 10 h in air yields finely divided $LiCoO_2$.

X-ray diffractograms of all the samples showed sharp well-defined peaks indicating high crystallinity and good hexagonal characteristics. The variation of the lattice parameters *a*, *c* and *c/a* with the TEA:sucrose ratio is shown in Table 1. A *c* value of 14.09 Å for the product prepared at the 1:8 ratio is close to the reported value of 14.06 Å for high-temperature $LiCoO_2$ [2]. Similarly, the *c/a* value for the 1:8 ratio sample agrees with the 4.99 Å reported for high-temperature $LiCoO_2$ [2]. The BET surface areas of the samples showed a nearly linear decrease from 2.99 m^2/g to 0.12 when the TEA:sucrose ratio was decreased form 1:1 to 1:16. TEA helps in the dispersion of the cations in the carbonaceous matrix, which is formed upon its carbonization. On the other hand, an increase in the amount of sucrose would lead to a swift rise in temperature in a narrow timeframe due to the combustion of sucrose. Thus, increased amounts of sucrose should lead to a sintering of the particles. According to Janbey et al. [3] sucrose forms a carbonaceous matrix upon decomposition, which acts as a substrate for the homogeneous distribution of the metal oxide phase. On calcination, the carbonaceous substrate is oxidized to carbon dioxide, leaving behind a finely divided oxide phase [3]. In our case, triethanolamine, with its three hydroxyl groups and nitrogen atom, and the polyhydroxy sucrose coordinate with the metal ions to form micelles in which the cations are trapped in an organic environment. The micelle formation hampers selective precipitation of the metal ions during evaporation of water from the solution. Upon heating, the organic moieties get partially carbonized, providing a substrate in which the metal ions find themselves embedded. Eventually, the metal nitrates oxidize the organic substrate, which acts as an internal fuel, yielding the desired product. The accompanying gas evolution helps break down large agglomerated particles.

The products were galvanostatically cycled at a 0.1 C rate in 2032-type coin cells with a lithium metal anode. The best results were obtained with the 1:8 TEA-sucrose product. Cycling between 3.0 and 4.3 V gave capacities of 156 and 153 mAh/g in the first and fifth cycles, respectively. A subsequent increase in the voltage range to 3.0 ~ 4.4 V gave capacities of 167 and 165 mAh/g in the sixth and tenth cycles, respectively. The performance of the sample was also compared with that of a commercial sample of $LiCoO_2$ (Comax) at a 0.2 C rate. It can be seen from Fig. 1 that the initial capacity of our sample (137 mAh/g) was higher than that of the commercial sample (132 mAh/g) and the cyclability at a 0.2 C rate between 3.0 and 4.2 V was also higher. For example, the number of cycles that the present sample could sustain before it reached a capacity retention level of 80% was 98, while for the same capacity retention the commercial sample could only sustain 68 cycles.

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References

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Table 1. Lattice parameters and BET surface areas for $LiCoO_2$ synthesized with different TEA:sucrose ratios.

TEA:Sucrose ratio	*a* (Å)	*c* (Å)	*c/a*	Surface area (m^2/g)
1:1	2.81	13.99	4.97	2.99
1:2	2.81	14.00	4.98	2.48
1:4	2.81	13.87	4.94	0.56
1:8	2.82	14.09	5.00	1.41
1:16	2.81	14.02	4.99	0.12

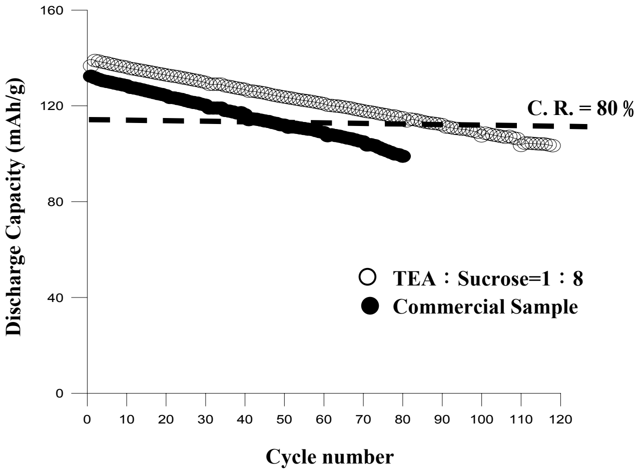

Fig. 1. Cycling performances of $LiCoO_2$ obtained with a TEA:sucrose ratio of 1:8 and a commercial $LiCoO_2$ at a 0.2 C rate between 3.0 and 4.2 V.