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The Role of the Electrically Conductive Agents in Lithium Transition Metal Oxides for Li-ion Batteries

Chang Woo Lee and Mun Soo Yun

Battery Research Group, Korea Electrotechnology Research Institute (KERI),
SeongJu-Dong, ChangWon, 641-120, S. Korea
Tel: +82-55-280-1666, Fax: +82-55-280-1590
E-mail: cwlee@keri.re.kr

In general, cathodes for Lithium secondary batteries [1-3] include carbon as a conductive agent that provides electron transfer between the Li metal oxide particles and the current collector. Basically the role of the conductive agent is order to enhance the electrode conductivity by filling the free spaces made by the grains of active material to form a continuous network until eventually the electrical conductivity approaches that of the conductive agent as well as allowing the close adhesion between Li^+ and active material by keeping the electrolytes[4-6]. Decrease of particle size of a conductive agent results in decreasing of ionic diffusion rate because of higher packing density, whereas contributes on improving for electrical contact between the lithium metal oxide and the conductive agent.

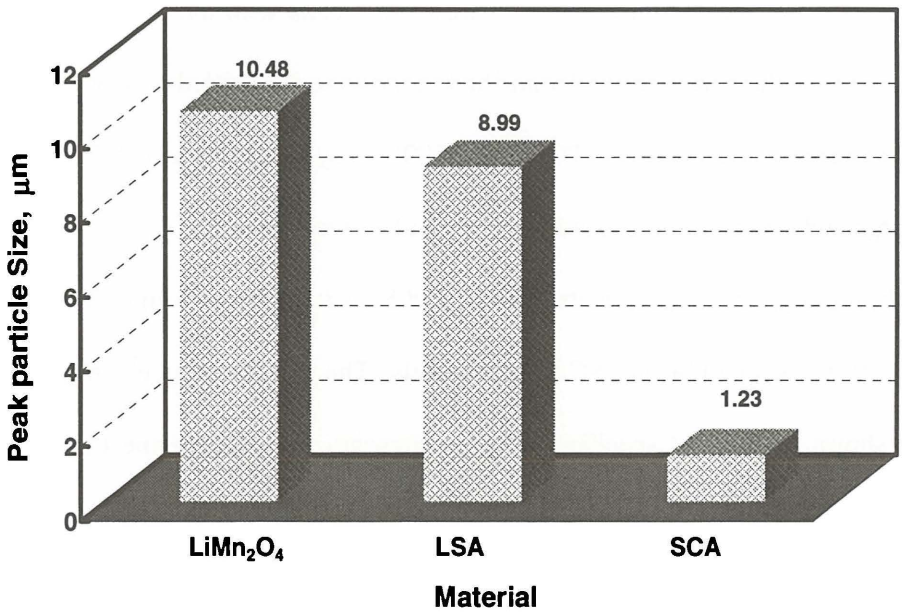

Fig. 1. The peak particle size of corresponding materials.

The main concern of this work is to investigate the influence of binary conductive agents for spinel $LiMn_2O_4$ cathodes with two different particle-sized conductive agents, in selection of commercialized available carbons. As results, the effect of binary conductive agents with different ratios is discussed based on electrochemical performances for $Li/LiMn_2O_4$ secondary batteries.

In order to investigate the role of the electrically conductive agents in lithium transition metal oxides, two different types of carbons as conductive agents were used. Also, spinel $LiMn_2O_4$ as a cathode active material and PVDF [Poly(vinylidene fluoride)] (Aldrich) as a binder were used in this study.

Fig. 1 shows the peak particle size of the $LiMn_2O_4$ active material and the electrically conductive agents indicated as LCA and SCA. The particle size measurement of conductive agents and spinel $LiMn_2O_4$ compound was performed by laser particle size analyzer (LPSA) (Mastersizer, Malvern).

The peak particle size of spinel $LiMn_2O_4$ active material is 10.48 ㎛. LCA and SCA demonstrate 8.99 ㎛ and 1.23 ㎛ in peak particle size, respectively, indicating in the order of $LiMn_2O_4$, LCA, and SCA as the peak particle size. We believed that free spaces could be formed by spinel $LiMn_2O_4$ active material, LCA, and current collector, simultaneously occupied by smaller particles of SCA. Fig. 2 shows the electrochemical performances for $Li/LiMn_2O_4$ cells with the binary conductive agents by different ratios after 20 cycles. To investigate the electrochemical performances of $Li/LiMn_2O_4$ cells with the binary conductive agents, 2032 coin-type cells (20 mm diameter, and 3.2 mm thickness) were assembled in dry room. These cells were galvanostatically cycled using a cycler (TOSCAT-3100U, Toyo system) at the C/5 current rate to cutoff voltages for charge and discharge of 4.5 and 3.5 V vs. Li/Li^+, respectively.

It is for the electrically conductive agents of LCA and SCA in different weight ratios. For example, L3S7 indicates for 30:70 wt. % of LCA and SCA, respectively. The $Li/LiMn_2O_4$ cell in the 3:7 weight ratios of LCA and SCA shows the highest specific discharge capacity. Particularly, the $Li/LiMn_2O_4$ cells with the binary conductive agents demonstrate significantly higher specific discharge capacities rather than in case of using SCA or LCA alone as single conductive agent. Here, the better electrochemical performances of $Li/LiMn_2O_4$ cells with the binary conductive agents are significantly ascribed to the facile ionic diffusion rate corresponding to the combination of larger particle-sized LCA. Fig. 3 shows specific discharge capacity vs. cycle numbers for Li/$LiMn_2O_4$ cells with the electrically conductive agents consisting of LCA and SCA by different ratios at room temperature.

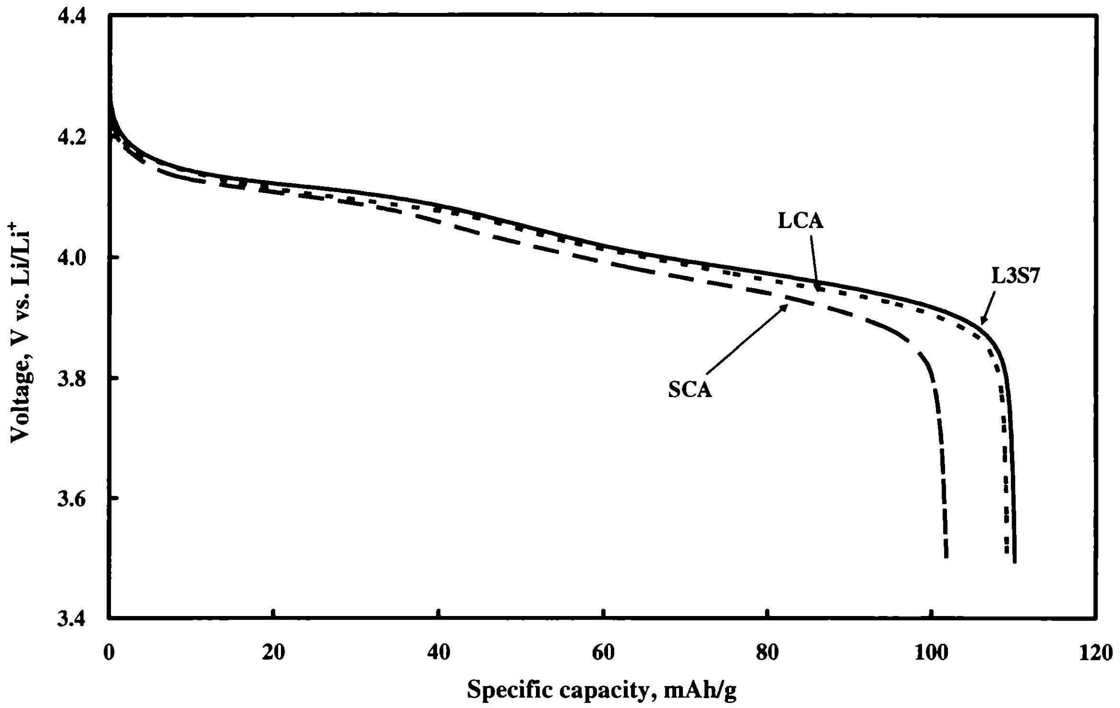

Fig. 2. Specific discharge capacities for Li/$LiMn_2O_4$ cells after 20 cycles with corresponding amount of the electrically conductive agents between 3.5 and 4.5V vs. Li/Li^+ at room temperature.

It can be seen from this figure that the tested cell with the binary conductive agents show good capacity retention with no any significant capacity loss during cycling when compared with the cases of using single conductive agents. In case of using single conductive agent, LCA shows higher specific discharge capacity and stable cycling behavior approximately after 10 cycles. Comparatively, L3S7 cell significantly demonstrates the stable cycle life during the number of cycles. Consequentially, SCA was relatively smaller in particle size, and the binary conductive agent in the 3:7 weight ratio of LCA and SCA shows the highest electrochemical performances in terms of specific discharge capacity and cycle life rather than in case of using single conductive agent.

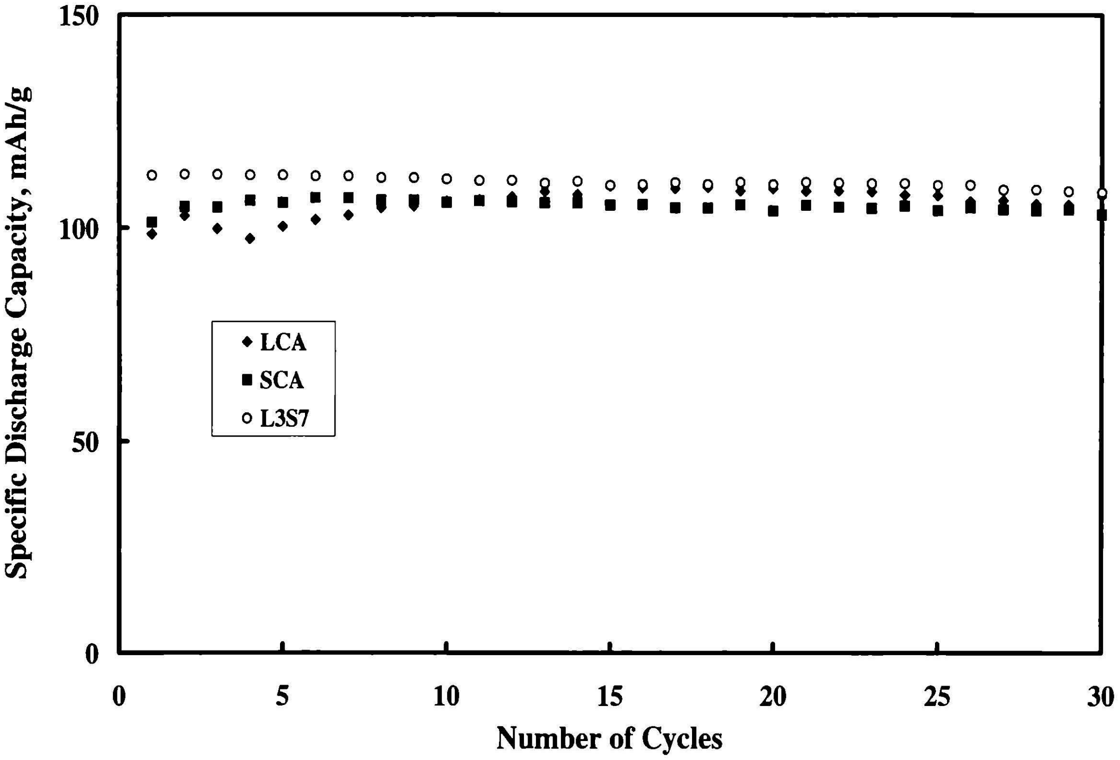

Fig. 3. Cycle life of $Li/LiMn_2O_4$ cells corresponding amount of the electrically conductive agents consisting of LCA and SCA.

Acknowledgment

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References

[1] G. B. Appetecchi, B. Scrosati, Electrochim. Acta, **43**(9), 1105 (1998).

[2] K. M. Abraham, D. M. Pasquariello, E. M. Willstaedt, J. Electrochem. Soc., **145**(2), 482 (1998).

[3] T. Ohzuku, A. Ueda, J. Electrochem. Soc., **141**(11), 2972 (1994).

[4] Jin K. Hong, Jong H. Lee, Seung M. Oh, J. Power Sources, **111**, 90 (2002).

[5] K. Kinoshita, Carbon: Electrochemical and Physical Properties, Wiley, NY, **Chap. 7** (1998).

[6] J. Lahaye, M. J. Wtterwald, J. Messit, J. Apple. Electrochem., **14**, 117 (1984).