Nanoparticles Formation Mechanism of Li-Mn Composite Oxides by Multiphase AC arc

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Abstract: Layered rock-salt type $LiMnO_2$ and spinel-type $LiMn_2O_4$ nanoparticles were successfully synthesized by a multiphase AC arc (MPA). A control of driving frequency of MPA improves selectivity of nanoparticles structure. High-speed visualization of fluctuated temperature field at different frequencies revealed the suppressed arc temperature fluctuation at higher frequency, resulting in preferable formation of $LiMnO_2$. Obtained remarks suggest feasibility of MPA for attractive Li-based nanoparticles production at high processing rate.

Keywords: thermal plasmas, high-speed visualization, lithium-ion battery

1. Introduction

Lithium metal oxides have attracted many researchers because of their unique properties such as materials for lithium ion batteries (LIB). Control of crystal structure for the lithium metal oxides are essential to enhance the battery characteristics. Spinel-type, layered rock-salt type, and olivine type materials are considered as suitable structure of cathode material due to its high mobility of lithium ion. In particular, spinel structured $LiMn_2O_4$ is one of promising high-voltage cathode materials for LIB due to its high theoretical energy density, low cost, and its good safety [1], while $LiMnO_2$ is also good candidate de to its excellent cycle life.

Thermal plasmas are expected to be utilized in mass-production process of attractive nanomaterials. Thermal plasmas can offer unique advantages: high enthalpy to enhance reaction kinetics, high chemical reactivity, rapid quenching rate in rage of 10^3-10^6 K/s, and selectivity of atmosphere in accordance with the required reaction. Recent researches revealed the feasibility of thermal plasma for LIB related nanoparticles production of $LiMn_2O_4$ [2], $LiNi_{0.5}Mn_{1.5}O_4$ [3], and so on. However, these works are limited in the utilization of induction thermal plasma. Thermal plasma sources at higher energy efficiency and larger processing capability are expected to be applied to mass production process in industrial field.

A multiphase AC arc (MPA) has been developed as one of the most attractive thermal plasma sources with large plasma volume at high energy efficiency [4]. The multiphase AC arc has been applied to a massive powder processing such as in-flight glass melting and nanomaterial production processes. Further recent works based on high-speed imaging technique revealed the fluctuation phenomena in MPA. However, there is no scientific reports on feasibility of MPA in nanomaterial production for LIB. The purpose of the present study is to synthesize nanoparticles of Li-Mn oxide composite by MPA. Another purpose is to investigate the formation mechanism by elucidating the temperature field.

2. Experiment

The schematic diagram of the MPA is shown in **Fig. 1**. It consists of 6 electrodes, arc chamber, vacuum pump, powder filter, and AC power supplies. These electrodes with a diameter of 6 mm were made of tungsten (98%) and cerium oxide (2%). The arc chamber was filled with argon gas. The electrodes are at an angle of 45 degree with regard to the horizontal plane. The ambient pressure was set at 100 kPa. Arc current for each electrode was fixed at 120A. The distance between the opposing electrodes was 52 mm. Argon gas was injected around each electrode at 5 L/min. The frequency was changed from 60Hz to 180Hz.

A powder mixture of Li_2CO_3 and MnO_2 was introduced into the plasma at a feed rate of 0.7 g/min. Molar ratio of Li to Mn was adjusted at 1:1. Synthesized nanoparticles were analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

High-speed camera with appropriate band-pass filters were utilized to visualize Li vapor as described in **Fig. 2**. Excitation temperature of was estimated by the relative intensity ratio method.

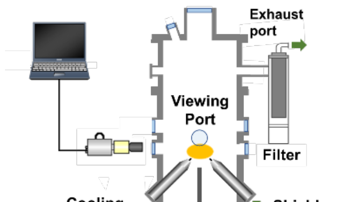

Fig. 1 Schematic diagram of multiphase AC arc generator.

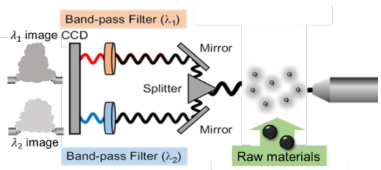

Fig. 2 Schematics of high-speed visualization system.

3. Results and Discussion

Figure 3 shows the XRD patterns of nanoparticles produced by MPA at each frequency condition. Results indicated that both spinel-type $LiMn_2O_4$ and layered rock-salt type $LiMnO_2$ was synthesized as major product, while Li_2CO_3 was also observed as minor product. The results also showed an increase in the fraction of $LiMnO_2$ and a decrease in the fraction of $LiMn_2O_4$ and Li_2CO_3 as the frequency was increased.

Representative TEM images of each prepared nanoparticles and corresponding particle size distributions are summarized in **Fig. 4**. Hexagonal shape of the nanoparticles was observed from TEM images. Additional SEM observation as well as our previous research suggests that the observed hexagonal shape corresponds to truncated octahedral structure of spinel $LiMn_2O_4$. This truncated structure is significantly different from the structure conventional obtained from other methods. This is due to their low surface energy [5]. Obtained results also indicated that the higher driving frequency leads to lower fraction of spinel nanoparticles. The reason why driving frequency has strong influence on nanoparticles formation is elucidated on the basis of the high-speed visualization of metal vapor in thermal plasma flow.

Figure 5 shows the fluctuated temperature field of MPA at different driving frequencies. Results clearly indicates that the higher frequency leads to constricted high temperature region in radial direction as well as significant extension in axial direction. Further analyses of the visualized temperature field indicate that an increase of driving frequency leads to higher temperature at suppressed temperature fluctuation.

Above results can be explained by two possible reasons. First reason is due to constriction of arc region. This originated from the suppression of arc fluctuation at higher frequency [4]. Second reason is due to the different flow field in MPA at different frequencies. Suppressed arc fluctuation at higher frequency improve flow uniformity in axial direction, while strong turbulence caused by arc fluctuation at lower frequency.

Increasing frequency leads to more uniform thermal history. Hence, the fraction of layered rock-salt $LiMnO_2$ with similar to initial composition becomes larger due to relatively more uniform history at higher frequency.

4. Conclusion

Nanoparticles of Li-Mn composite oxide were successfully synthesized as major product by the multiphase AC arc. High-speed visualization technique revealed that the driving frequency has strong role on controlling arc fluctuation and corresponding high temperature field. Obtained remarks suggests that thermal plasma synthesis enables to produce attractive electrode materials for lithium-ion battery at high-productivity.

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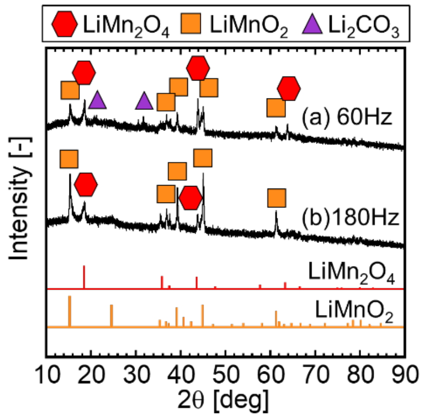

Fig. 3 XRD spectrum chart of produced nanoparticles at frequencies of (a) 60 Hz and (b) 180hz.

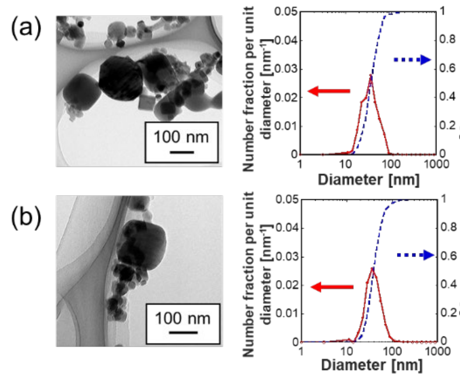

Fig. 4 Representative TEM images and size distributions with different driving frequencies: (a) 60Hz and (b) 180Hz.

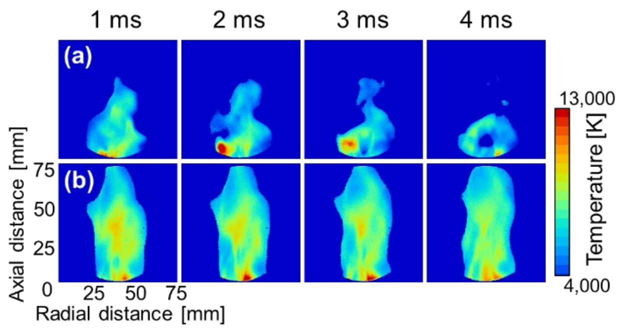

Fig. 5 Visualized temperature distributions at different frequencies; (a) 60Hz and (b) 180Hz.

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