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Effects of types of drying control chemical additives on the morphologies and electrochemical properties of $Li_4Ti_5O_{12}$ anode powders prepared by spray pyrolysis

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ABSTRACT

The various types of drying control chemical additives are applied to control the morphological and electrochemical characteristics of the $Li_4Ti_5O_{12}$ powders prepared by spray pyrolysis. The $Li_4Ti_5O_{12}$ powders obtained from the spray solutions with formamide, *N*,*N*-dimethylformamide, *N*-methylacetamide and 1,4-dioxane have dense structures and fine sizes. On the other hand, the $Li_4Ti_5O_{12}$ powders obtained from the spray solution with glycerol have hollow structure and large size. The $Li_4Ti_5O_{12}$ powders obtained from the spray solutions with formamide, *N*,*N*-dimethylformamide and 1,4-dioxane have high initial discharge capacities of 167, 166 and 163 mAh/g at a constant current density of 0.1 C. The discharge capacity of the $Li_4Ti_5O_{12}$ powders obtained from the spray solution with formamide is 95% of the initial discharge capacity after 60 cycles.

1. Introduction

$Li_4Ti_5O_{12}$ has good Li^+ insertion and de-insertion reversibility with negligible structure change (the so-called "zero-strain" insertion material) during charge–discharge cycling [1–6]. $Li_4Ti_5O_{12}$ can be used as an anode coupled with high potential cathode materials ($LiMn_2O_4$ or $LiCoO_2$) to provide a cell with an operating voltage of about 2.5 V [7]. The characteristics of $Li_4Ti_5O_{12}$ powders synthesized by various preparation processes were investigated [8–18].

Spray pyrolysis, which is one of the gas phase reaction method, was applied to the preparation of various types of cathode materials for lithium secondary batteries [19–22]. The characteristics of the $Li_4Ti_5O_{12}$ powders prepared by spray pyrolysis were also studied [23,24]. The morphologies of the powders prepared by spray pyrolysis were affected by the preparation conditions and the types of spray solution. Various types of organic materials were used as additives to control the morphologies of the cathode materials [25–27]. Drying control chemical additive (DCCA) was also applied to the preparation of the cathode powders in the spray pyrolysis. *N*,*N*-dimethylformamide (DMF) used as DCCA improved the morphological and electrochemical properties of the $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode powders prepared by spray pyrolysis [26].

In this study, various types of DCCA material are used to control the morphological and electrochemical properties of the $Li_4Ti_5O_{12}$ anode powders prepared by spray pyrolysis.

2. Experimental

The spray pyrolysis system consists of a droplet generator, a quartz reactor, and a powder collector. A 1.7-MHz ultrasonic spray generator with six vibrators was used to generate a large amount of droplets, which are carried into the high-temperature tubular reactor by a carrier gas. The droplets and powders evaporated, decomposed, and/or crystallized in the quartz reactor. The length and diameter of the quartz reactor were 1200 and 50 mm, respectively. The reactor temperature was 800 °C. The flow rate of air used as the carrier gas was 30 L min^{-1}, and the residence time of the powders inside the reactor was 1.1 s. The precursor solution was prepared by dissolving lithium nitrate ($LiNO_3$), titanium(IV) tetraisopropoxide (TTIP, $Ti[OCH(CH_3)_2]_4$), citric acid (CA) and ethylene glycol (EG) in distilled water using small amount of nitric acid. The overall solution concentration of Li and Ti components was 0.5 M. The concentrations of the CA and EG used as polymeric precursors were each 0.1 M.

Formamide (FA), *N*-methylformamide (MF), *N*,*N*-dimethylformamide (DMF), *N*-methylacetamide (MA), acetonitrile, 1,4-dioxane, 1-dodecanol and glycerol were used as the DCCA materials to control the drying rate of droplets inside the hot-wall reactor. The concentration of DCCA was 0.5 M. The as-prepared powders obtained by spray pyrolysis were post-treated at a temperature of 800 °C for 12 h in air atmosphere.

The crystal structures of the as-prepared and post-treated powders were investigated by X-ray diffractometry (XRD, RIGAKU DMAX-33) using Cu Kα radiation ($\lambda = 1.5418 \times 10^{-10}$ m). The morphological characteristics of the powders were investigated using scanning electron microscopy (SEM, JEOL JSM-6060). The anode electrode was made of 12 mg of $Li_4Ti_5O_{12}$ compounds mixed with 4 mg of a conductive binder (3.2 mg of teflonized acetylene black and 0.8 mg of graphite). The lithium metal and polypropylene film were used as the counter electrode and the separator, respectively. The electrolyte (TECHNO Semichem. Co.) was 1 M $LiPF_6$ in a 1:1 mixture by volume of EC/DMC. The entire cell was assembled in a glove box

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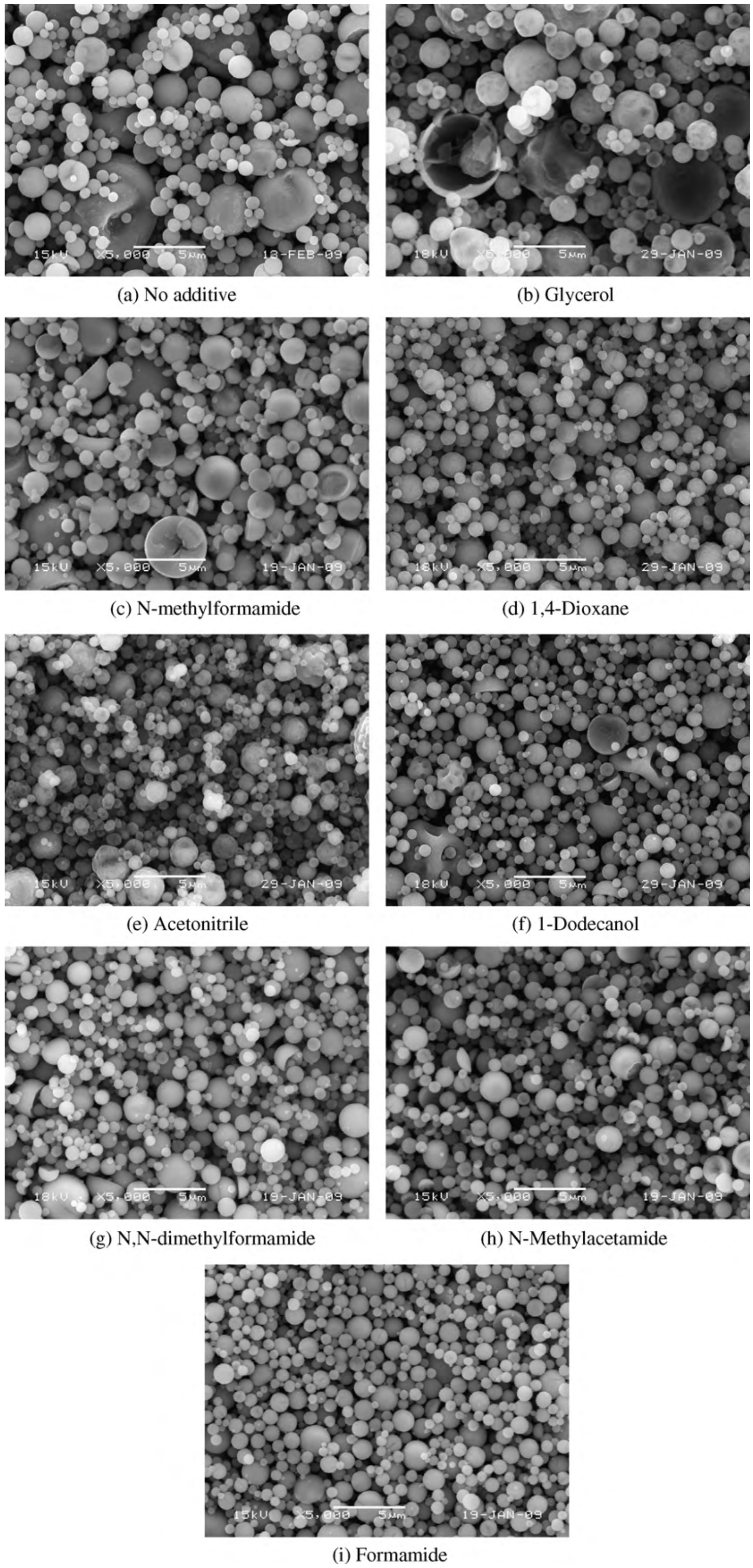


Fig. 1. SEM images of the precursor powders prepared from the spray solutions with various types of DCCA.

under an argon atmosphere. The charge/discharge characteristics of the samples were measured through cycling in the 1–2.5 V potential range.

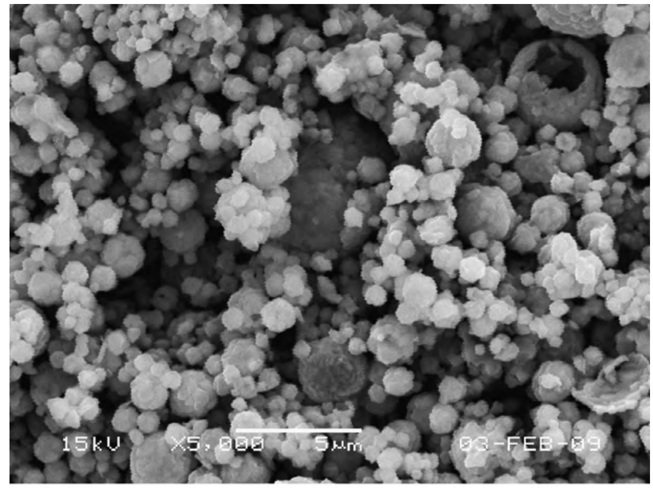
3. Results and discussion

The addition of DCCA materials to the spray solution improved the morphological characteristics of the as-prepared and post-treated $Li_4Ti_5O_{12}$ anode powders prepared by spray pyrolysis. Fig. 1 shows the SEM images of the as-prepared powders obtained by spray pyrolysis from the spray solutions with various types of DCCA material. The powders obtained from the spray solution without DCCA material had spherical shape and broad size distribution. The different morphologies of the powders formed from the droplets with different sizes increased the size distribution of the powders. The mean size of the powders as shown in Fig. 1(a) was 1.80 μm. DCCA materials were added to the polymeric spray solutions containing citric acid and ethylene glycol. The morphologies of the as-prepared powders were affected by the types of DCCA material added to the spray solutions. DCCA materials except glycerol improved the morphological characteristics of the as-prepared powders. The as-prepared powders formed from the spray solution with glycerol had hollow structure. The mean size of the powders as shown in Fig. 1(b) was 1.99 μm. The as-prepared powders obtained from the spray solutions with MF, 1,4-dioxane, acetonitrile, and 1-dodecanol had finer sizes than those obtained from the spray solutions without DCCA and with glycerol. However, the as-prepared powders as shown in Fig. 1(c)–(f) had hollow inner structure. On the other hand, the as-prepared powders obtained from the spray solutions with formamide, DMF, and MA had dense structures. The mean sizes of the as-prepared powders obtained from the spray solutions with MF, 1,4-dioxane, acetonitrile, 1-dodecanol, DMF, MA, and formamide were 1.55, 1.39, 1.37, 1.30, 1.23, 1.10, and 1.01 μm, respectively. The as-prepared powders obtained from the spray solution with formamide had the smallest size because of their dense structure. The geometric standard deviations of the as-prepared powders obtained from the spray solutions with glycerol, MF, 1,4-dioxane, acetonitrile, 1-dodecanol, DMF, MA, and formamide were 1.62, 1.60, 1.65, 1.52, 1.37, 1.55, 1.44, and 1.50, respectively.

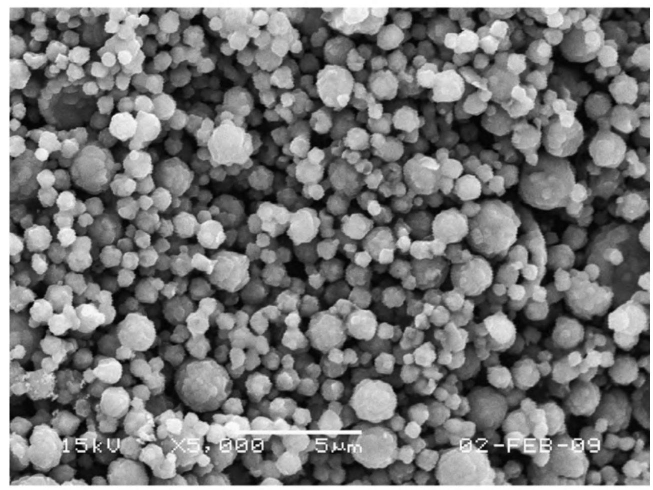
The spherical shapes of the as-prepared powders were maintained after post-treatment at 800 °C, in which the $Li_4Ti_5O_{12}$ powders had high initial discharge capacity and good cycle property. However, the morphologies of the $Li_4Ti_5O_{12}$ powders were affected by the morphologies of the as-prepared powders. The post-treated $Li_4Ti_5O_{12}$ powders formed from the as-prepared powders with dense structure had more dense structure than those formed from the ones with hollow morphology. Fig. 2 shows the SEM images of the post-treated $Li_4Ti_5O_{12}$ powders obtained from the spray solutions with glycerol and formamide. The $Li_4Ti_5O_{12}$ powders formed from the spray solution with formamide had spherical shape, dense structure and non-aggregation characteristics.

Fig. 3 shows the XRD patterns of the post-treated $Li_4Ti_5O_{12}$ powders obtained from the polymeric spray solutions with formamide, 1,4-dioxane and glycerol. All the diffraction peaks of the $Li_4Ti_5O_{12}$ powders obtained from the polymeric spray solutions with formamide and 1,4-dioxane can be indexed based on a face centered cubic spinel structure with a *Fd3m* space group [3,4]. On the other hand, the $Li_4Ti_5O_{12}$ powders obtained from the spray solution with glycerol had main peaks of $Li_4Ti_5O_{12}$ phase and two extra diffraction peaks at $2\theta = 27.4°$ and $54.3°$, indicating that the presence of a small amount of rutile TiO_2. The mean crystallite sizes of the $Li_4Ti_5O_{12}$ powders obtained from the spray solutions with formamide and 1,4-dioxane measured by Scherrer's equation were 70 and 62 nm.

Fig. 4 shows the initial charge/discharge capacities of the $Li_4Ti_5O_{12}$ powders obtained from the spray solutions with different



(a) Glycerol



(b) Formamide

Fig. 2. SEM images of the post-treated $Li_4Ti_5O_{12}$ powders prepared from the spray solutions with various types of DCCA.

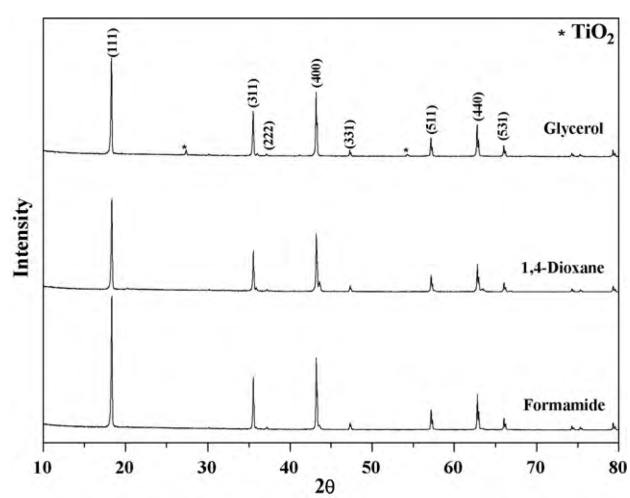


Fig. 3. XRD patterns of the post-treated $Li_4Ti_5O_{12}$ powders prepared from the spray solutions with various types of DCCA.

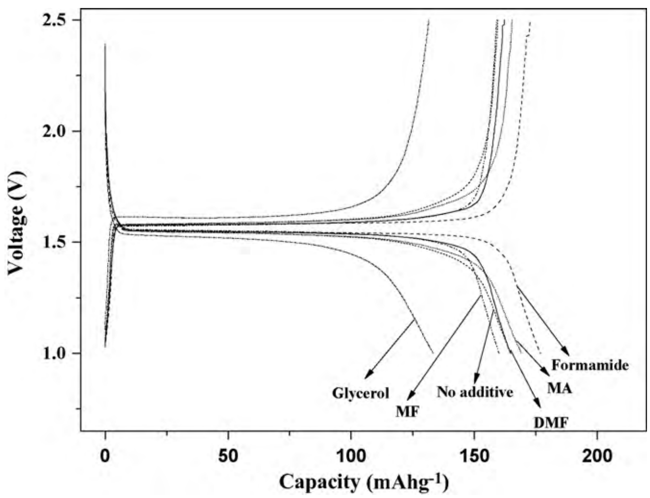


Fig. 4. Initial charge/discharge curves of the $Li_4Ti_5O_{12}$ powders prepared from the spray solutions with various types of DCCA.

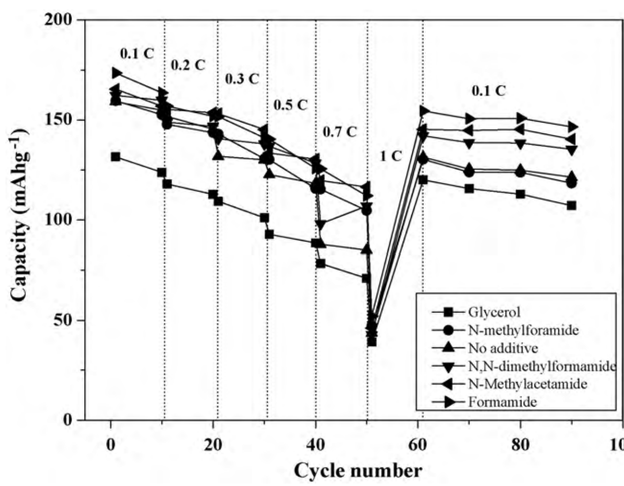


Fig. 5. Cycle properties of the $Li_4Ti_5O_{12}$ powders prepared from the spray solutions with various types of DCCA.

DCCAs. The $Li_4Ti_5O_{12}$ powders obtained from the spray solutions with formamide, MF, and DMF had high initial discharge capacities of 174, 165 and 162 mAh g^{-1} at a constant current density of 0.1 C. On the other hand, the $Li_4Ti_5O_{12}$ powders obtained from the spray solution with glycerol had low initial discharge capacity of 131 mAh g^{-1} at a constant current density of 0.1 C. The low initial discharge capacity of the powders obtained from the spray solution with glycerol due to the formation of TiO_2 impurity phase by evaporation of lithium component. Fig. 5 shows the cycle stabilities of the $Li_4Ti_5O_{12}$ powders at various current densities. The $Li_4Ti_5O_{12}$ powders obtained from the spray solutions with different DCCAs had similar cycle properties at various current densities irrespective of the morphologies of the powders. After 60 cycles, the discharge capacities of the $Li_4Ti_5O_{12}$ powders obtained from the spray solutions with formamide and DMF were 95 and 92% of the initial discharge capacities at a constant current density of 0.1 C, respectively.

4. Conclusion

The effects of drying control chemical additive dissolved to the spray solutions on the characteristics of $Li_4Ti_5O_{12}$ powders prepared by spray pyrolysis are investigated. The types of drying control chemical additive (DCCA) affect the morphologies, crystal structures and cycle properties of the as-prepared and post-treated $Li_4Ti_5O_{12}$ powders. The $Li_4Ti_5O_{12}$ powders prepared from the spray solutions with appropriate DCCA materials have dense structure, fine size, pure crystal structure and high discharge capacity.

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