



Short communication

Effects of drying control chemical additive on properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powders prepared by spray pyrolysis

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ABSTRACT

High-density $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders comprising spherical particles are prepared by spray pyrolysis from a solution containing dimethylacetamide (drying control chemical additive) and citric acid and ethylene glycol (organic additives). The prepared powders have high discharge capacities and good cycle properties. The optimum concentration of dimethylacetamide is 0.5 M. The addition of dimethylacetamide to the polymeric spray solutions containing citric acid and ethylene glycol helps in the effective control of the morphology of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders. At a constant current density of 0.17 mA g^{-1} , the initial discharge capacities of the powders obtained from the spray solution with and without the organic additives are 171 and 167 mAh g^{-1} , respectively.

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1. Introduction

Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is a promising candidate for use as a negative electrode material in lithium-ion batteries [1,2]. The excellent cycle performance and long life of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode makes it suitable for use as the negative electrode in large-scale applications, particularly in all-solid-state lithium-ion batteries and hybrid supercapacitors [3]. The electrode shows a voltage plateau of 1.56 V against a lithium electrode. The theoretical specific capacity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode is 175 mAh g^{-1} , and its practical specific capacity is very high ($150\text{--}160 \text{ mAh g}^{-1}$) even after 100 deep-discharge cycles. The cubic symmetry of the parent spinel is unaffected by lithiation during the insertion and deletion of Li^+ ions; the lattice parameter (8.36 \AA) and unit-cell volume are also virtually unchanged by the phase transition [4–9].

Various methods such as the Pechini method, the emulsion method, hydrothermal decomposition, and co-precipitation as well as sol-gel reactions and other synthesis routes have been developed for producing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powders with excellent electrochemical properties [10–15]. On the other hand, the characteristics of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powders prepared by gas-phase reactions have not been investigated in detail. Spray pyrolysis, which is a gas-phase reaction, has been used for the preparation of various types of electrode materials that can be used in lithium-ion batteries.

The performance of lithium-ion batteries is strongly affected by the properties of the powder materials used for constructing the electrodes, such as composition, morphology, specific surface-area, and crystallinity [16–19]. With respect to the powder morphology, spherical powders with a dense structure show better electrochemical performance than powders with irregular morphology and a hollow structure because the former minimizes diffusion pathway lengths and gives improved electrode properties through higher packing efficiencies [20–23]. The use of negative powders comprising fine-sized particles as electrode materials has been intensively investigated for improving the capacity and power output of lithium-ion batteries.

In this study, high-density $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powders that are comprised of spherical particles are prepared by spray pyrolysis. An amide-type drying control chemical additive (DCCA) is added to the spray solution to improve the morphology of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders. The addition of polymeric precursors to the spray solution along with the DCCA further improves the electrochemical properties of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders.

2. Experimental

The spray pyrolysis system consisted of a droplet generator, a quartz reactor, and a particle collector [24]. A 1.7-MHz ultrasonic spray generator with six vibrators was used to generate a large number of droplets, which were conveyed to the high-temperature tubular reactor by a carrier gas. The droplets and particles were evaporated, decomposed, and/or crystallized in the quartz reactor. The length and diameter of the quartz reactor

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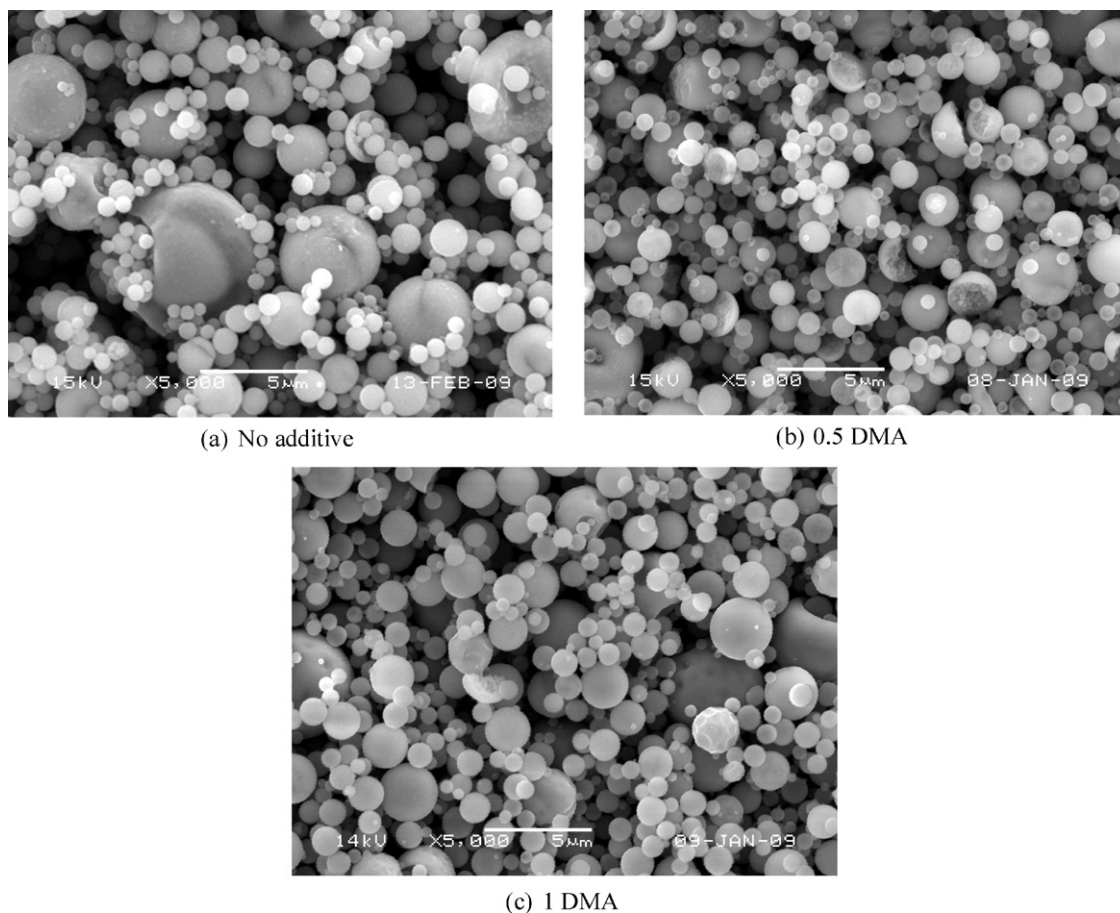


Fig. 1. SEM images of precursor powders obtained by spray pyrolysis.

were 1200 mm and 50 mm, respectively. The reactor temperature was maintained at 800 °C. The flow rate of air used as the carrier gas was 30 L min⁻¹. The precursor solution was prepared by dissolving lithium nitrate (LiNiO₃, Aldrich) and titanium tetraisopropoxide (TTIP, Ti(OCH(CH₃)₂)₄; Junsei) in distilled water with an appropriate amount of nitric acid. The overall concentration of the lithium and titanium components in the solution was 0.5 M. The DCCA, citric acid (CA) and ethylene glycol (EG) were added to the spray solution to control the morphology of the precursor powders. Dimethylacetamide (DMA) served as the DCCA. The concentration of DMA was increased from 0.1 to 1 M. The concentrations of CA and EG, which were employed as polymeric precursors, were changed from 0.05 to 0.3 M. The precursor powders obtained by spray pyrolysis were post-treated at 800 °C for 12 h in an air atmosphere. The yield of the spherical shape Li₄Ti₅O₁₂ powders was 10 g h⁻¹.

The crystal structures of the post-treated powders were investigated by X-ray diffractometry (XRD, Rigaku DMAX-33). The morphological characteristics of the powders were investigated by means of scanning electron microscopy (SEM, JEOL JSM-6060). The surface areas of the powders were measured by the Brunauer–Emmett–Teller (BET) method with N₂ gas as the adsorbate. The thermal properties of the prepared Li₄Ti₅O₁₂ negative powders were investigated by thermogravimetric–differential thermal analysis (TG–DTA) in the temperature range of 40–600 °C (heating rate: 10 °C min⁻¹). The initial capacities and cycle properties of the prepared Li₄Ti₅O₁₂ negative powders were measured. The electrode was fabricated using 12 mg of Li₄Ti₅O₁₂ and 4 mg of TAB (TAB is a mixture of 3.2 mg of teflonized acetylene black and 0.8 mg of binder). The TAB–Li₄Ti₅O₁₂ mixture was pressed between two aluminum plates and then vacuum-dried at 120 °C overnight.

Lithium metal and a polypropylene film were used as the negative electrode and the separator, respectively. The electrolyte (Techno Semichem. Co.) was 1 M LiPF₆ in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The entire cell was assembled under an argon atmosphere in a glove box. The electrochemical properties of the Li₄Ti₅O₁₂ negative powders were measured through cycling in the 1–2.5 V potential range at different current densities.

3. Results and discussion

The effect of DMA on the morphologies of the precursor powders obtained by spray pyrolysis is shown in Fig. 1. The precursor powders prepared from the spray solution without DMA are comprised of large particles with a broad size-distribution. The precursor powders obtained under severe preparation conditions comprised hollow particles, and hence, both the mean size and the size distribution of the particles increased. The residence time of the droplets or powders in the hot-wall reactor is 1.1 s. The addition of DMA to the spray solution improves the morphological characteristics of the precursor powders. The hollowness of the particles in the precursor powders decreases when DMA is used to control the drying rate of the droplets. The precursor powders prepared from the spray solution containing 0.5 M DMA are denser than those prepared from a spray solution containing 1 M DMA. The mean size of the powders shown in Fig. 1(a), (b) and (c) is 2.4, 1.4 and 1.7 μm, respectively.

The CA and EG polymeric precursors were added to the DMA-containing spray solution to improve the morphology of the precursor powders. The concentration of DMA was fixed at 0.5 M.

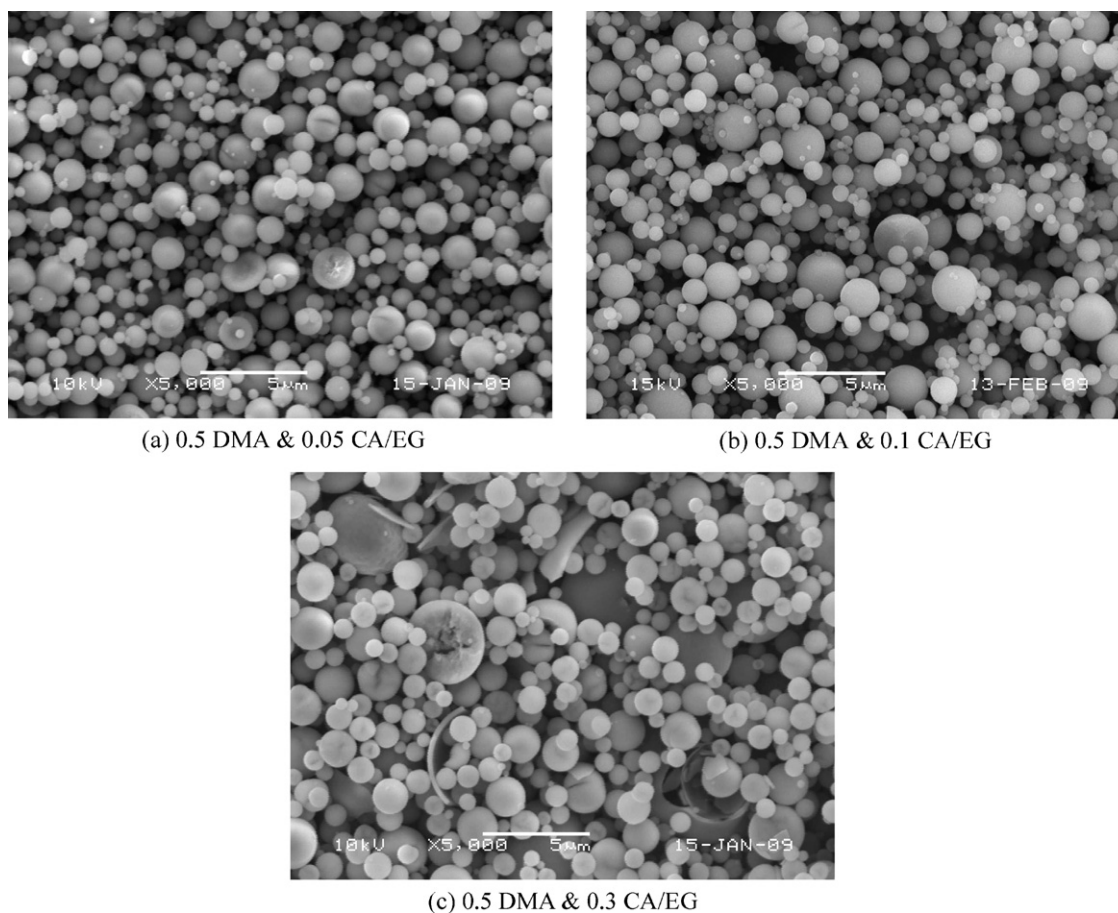


Fig. 2. SEM images of precursor powders prepared from spray solutions with different concentrations of CA and EG.

The morphologies of the precursor powders prepared from spray solutions with different concentrations of CA and EG are presented in Fig. 2. The precursor powders prepared from spray solutions in which the CA and EG concentrations are less than 0.1 M are dense and comprised of fine-sized spherical particles. Addition of CA and EG to the solution helps to improve the morphologies of the precursor powders, as shown in Fig. 1(a) and Fig. 2(b). In the hot-wall reactor, CA is esterified by EG to afford high-molecular-weight polymers. The addition of DMA (as the DCCA) promotes in effective control of the morphology of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders in the highly viscous polymeric spray solutions. Precursor powders formed from spray solutions with high concentrations of CA and EG are comprised of hollow particles, as shown in Fig. 2(c). The high rate of gas evolution from the decomposed polymers results in the formation of precursor powders of hollow particles. On the basis of these observations, the optimum concentrations of both CA and EG are determined to be 0.1 M. The mean sizes of the powders shown in Fig. 2(a), (b) and (c) are 1.11, 0.92 and 1.5 μm , respectively.

The pore-size distributions of the precursor powders analyzed by the Barrett–Joyner–Halenda (BJH) method are shown in Fig. 3. The precursor powders obtained from the spray solution without the additive have a large pore volume of meso (2–5 nm) pores. By contrast, dense precursor powders comprising particles with a small pore volume are obtained from the spray solution containing DMA, CA and EG, as shown in Fig. 2(b). The BET surface areas of the precursor powders obtained from the spray solutions with and without the additives are 2.3 and 2.7 m^2g^{-1} , respectively.

The TG and DTA curves of the precursor powders shown in Fig. 2(b) are given in Fig. 4. As seen from the TG curve, the total

weight loss of the precursor powders obtained at 800 °C is 8.3 wt.%. The thermal decomposition of the precursor powders occurs in three main steps. In the first step (between room temperature and 150 °C), the weight loss is mainly due to the vapourization of adsorbed water. This weight loss corresponds to an endothermic peak at around 100 °C on the DTA curve. The weight loss in the second step (150–261 °C) is 2.8 wt.%, and this is attributed to the decomposition of the undecomposed lithium and titanium precursors. The third weight loss step is observed from 261 to 400 °C. The

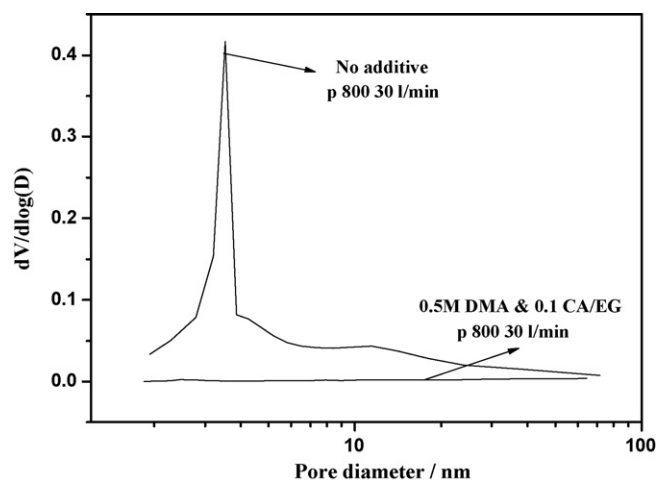


Fig. 3. Pore-size distributions of precursor powders prepared from spray solutions with and without organic additives.

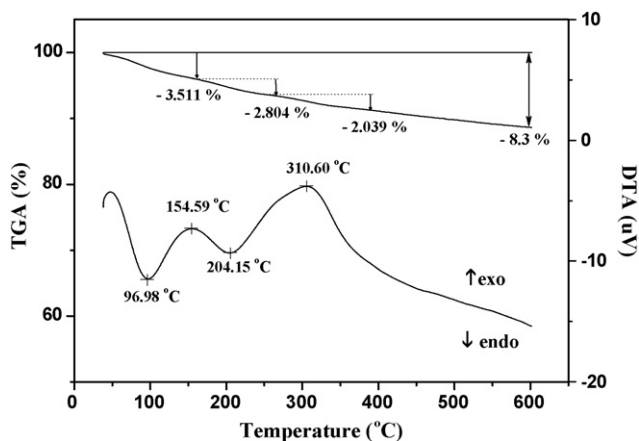


Fig. 4. TG/DTA curves of precursor powders prepared from spray solutions with organic additives.

weight loss in this region is due to the decomposition of the carbon components formed by the incomplete decomposition of DCCA and the organic polymers.

The SEM images of the post-treated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powders obtained from the spray solutions containing DMA and the organic additives (CA and EG) are presented in Fig. 5. The precursor powders obtained by spray pyrolysis were post-treated at 800°C . The spherical morphology of the particles in the precursor powders is retained after the post-treatment. Some of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powder samples obtained from the spray solutions containing low and high concentrations of the organic additives are comprised of

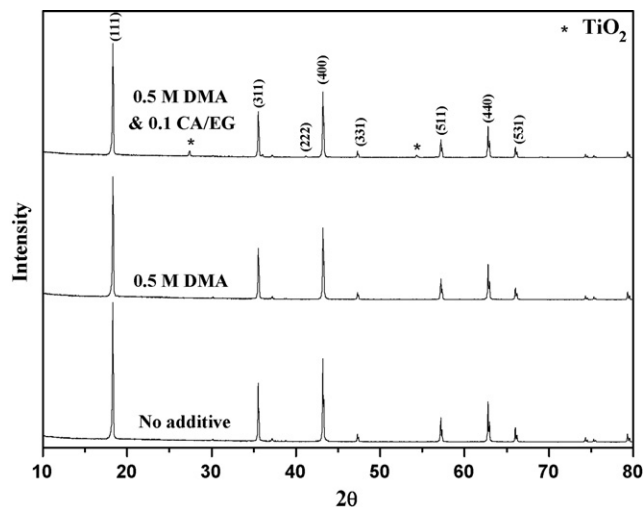
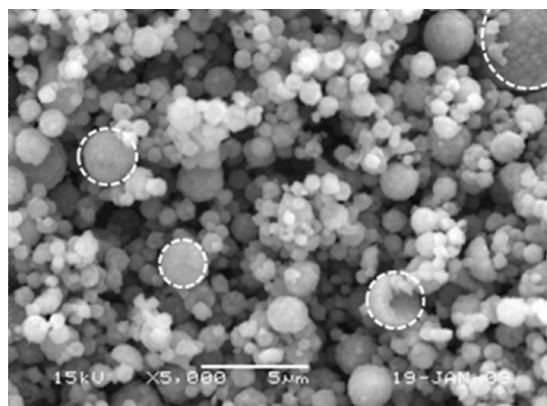


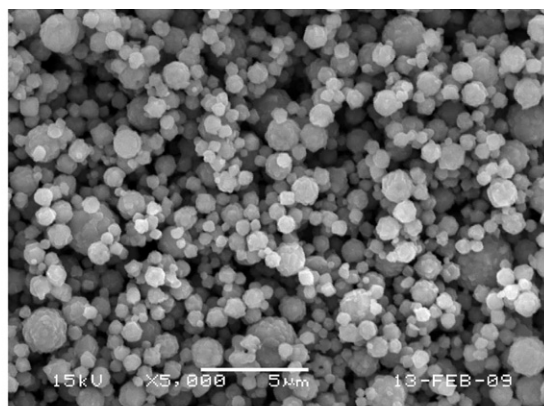
Fig. 6. XRD patterns of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders prepared from spray solutions with and without organic additives.

hollow particles, as shown by the circles in Fig. 5(a) and (c). On the other hand, the particles in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powders obtained from the spray solution in which the concentrations of both CA and EG are 0.1 M lose their hollow morphology during the post-treatment. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powders shown in Fig. 5(b) have non-aggregation characteristics.

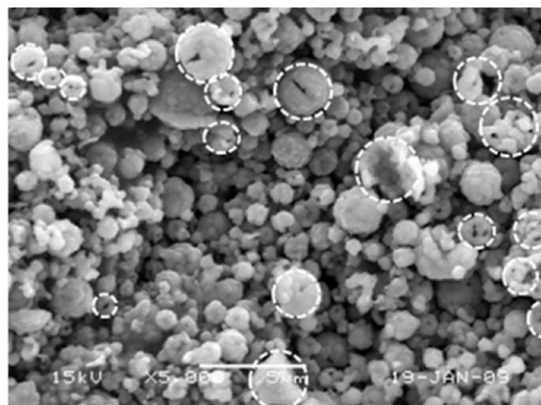
The XRD patterns of the post-treated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders obtained from the spray solutions with and without the additives



(a) 0.5 M DMA & 0.05 M CA/EG



(b) 0.5 M DMA & 0.1 M CA/EG



(c) 0.5 M DMA & 0.3 M CA/EG

Fig. 5. SEM images of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders prepared from spray solutions with different concentrations of CA and EG.

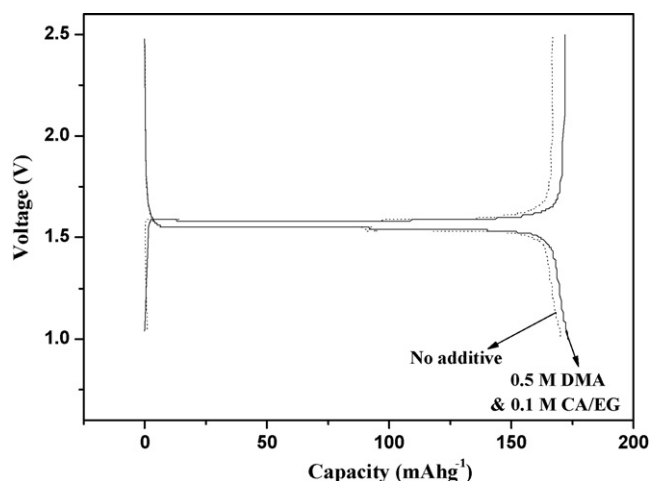


Fig. 7. Initial charge–discharge curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders prepared from spray solutions with and without organic additives.

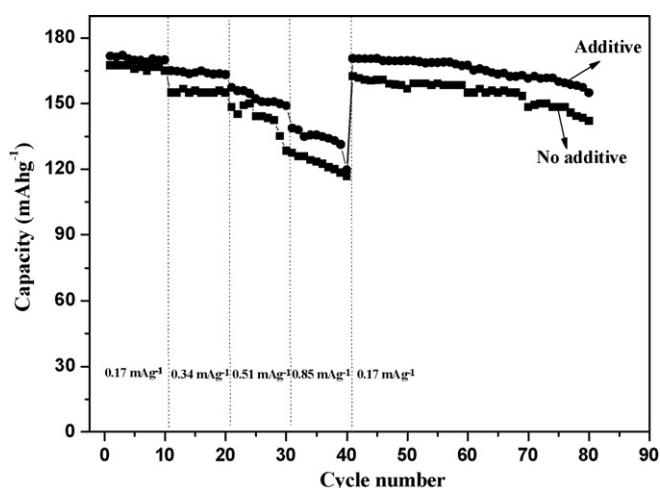


Fig. 8. Current density performances of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powders prepared from spray solutions with and without organic additives.

are given in Fig. 6. The powders prepared from the spray solutions containing DMA but not CA and EG are single-phase, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$. By contrast, the XRD patterns of the powders prepared from the spray solution containing DMA, CA and EG show small impurity peaks that are attributable to rutile TiO_2 in addition to the main peaks due to the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase. The temperature of the powders increases because of the heat released during the decomposition of the organic additives; this leads to the evaporation of a small amount of the lithium component from the powders and the formation of TiO_2 as the impurity phase. The mean crystallite sizes of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders calculated using Scherrer's equation vary from 56 to 70 nm depending on the type of spray solution used.

The initial charge/discharge capacities of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powders formed from spray solutions with and without the organic additives are shown in Fig. 7. At a constant current density of 0.17 mA g^{-1} , the initial discharge capacities of the powders obtained from the spray solutions with and without the organic additives are 171 and 167 mAh g^{-1} , respectively. The presence of TiO_2 does not cause a decrease in the discharge capacity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders formed from the spray solution containing the organic additives.

Fig. 8 shows the cycle properties of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powders when the current density is increased from 0.17 to 0.85 mA g^{-1} . In this current density range, the cycle properties of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powders formed from the spray solution containing DMA, CA and EG are better than those of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders formed from the spray solution without the organic additives. The cycle properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powders with and without organic additives at a constant current density of 0.7 mA g^{-1} after 40th cycle test by changing current density are also given in Fig. 8. The discharge capacities of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powders prepared from the spray solution without the organic additives decrease from 162 to 142 mAh g^{-1} by the 40th cycle. The discharge capacities of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powders prepared from the spray solution containing the organic additives decrease from 170 to 155 mAh g^{-1} by the 40th cycle. After 40 cycles, the discharge capacities of the powders formed from the spray solutions with and without the organic additives are 91 and 87% of the initial discharge capacities, respectively.

4. Conclusions

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powders are prepared by pyrolysis from solutions with and without organic additives (CA and EG). DMA is used as the DCCA for efficient control of the morphology of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders during spray pyrolysis. The XRD patterns of the powders prepared from the spray solution with the organic additives show small impurity peaks that are attributable to rutile TiO_2 in addition to the main peaks for the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase. The presence of TiO_2 impurity phase does not, however, cause a decrease in the discharge capacity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders formed from the spray solution with the organic additives. Dense $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative powders comprising spherical particles have a high discharge capacity and good cycle properties.

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