

Nano electronically conductive titanium-spinel as lithium ion storage negative electrode

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Abstract

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared by a solid-state reaction of ternary precursor materials TiO_2 , Li_2CO_3 and carbon. The precursors were mixed by two methods—a dry and wet process. Different types of carbons (carbon black, high-surface-area carbon, graphite and carbonized polymer) were used. The particle shape and size of the product were connected to the carbon type used in the synthesis. The electrochemical performance and the role of particle shape and size were investigated. The weight losses of ternary powder was monitored by TGA to establish the optimum synthesis temperature. XRD diffraction was used to study the TiO_2 residue in the final powder.

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1. Introduction

The emerging market for hybrid vehicles (HEVs) presents a challenge to identify low-cost materials with high power performance. A key element in HEVs is the battery which must have high power capability. On the other hand, energy density is reduced for this application compared to that required for pure electric vehicles (Es). A metal oxide, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, is a promising candidate as a negative electrode in solid, liquid and gel Li-ion batteries [1–10] and for hybrid supercapacitors [5,13,14,15]. For Li-ion batteries, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be used with high-voltage cathodes (5 V) as LiCoPO_4 [11], or 4 V cathodes as LiMn_2O_4 , LiCoO_2 and with a 3.5 V cathode, LiFePO_4 [12]. For use in HEVs, the major concern is safety. The mid-discharge voltage of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ close to 1.55 V versus Li^+/Li is very promising for a large number of battery applications [4,5]. The electrochemical activity occurs at a voltage higher than 1.0 V. Thus, the electrode does not experience the passivation of carbon materials and their inevitable electrolyte reaction. In this work, we report on the synthesis of a zero-strain insertion material with carbon additives. The influence of the carbon structure, particle morphology and particle size were investigated. The intent of the present paper is to extend our previous studies [13,14]

on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by providing a systematic analysis of a series of materials with different microstructures and morphologies obtained by a new synthesis procedure.

2. Experimental

The starting materials, TiO_2 -anatase and Li_2CO_3 , were commercially available with purities of 99 and 99.5%, respectively. A mixture of TiO_2 and Li_2CO_3 (molar ratio Ti/Li of 2.27) was prepared by three methods. Method A: precursors were mixed by jar milling in the presence of a liquid solvent such as acetone or water. Then the mixed powder was separated from the solvent by filtering and dried at 120 °C for 24 h. The powder was heated at 850 °C in air or N_2 to form the product. Method B: the proportion of TiO_2 and Li_2CO_3 was the same as in Method A but with 20% by weight of polymer such as PEO based in acetone or water. After filtration and drying, the powder was heated at 850 °C for 12 h in an air or N_2 . Method C: the same method as B, except, changed from 20 wt.% polymer to 10 wt.% polymer plus 3% W Shawinigan carbon black.

In the second method (B), carbon was added to the starting materials (TiO_2 , Li_2CO_3) to make a ternary mixture. The homogeneous mixed phases of the binary and ternary compositions were obtained by high-energy ball milling. In this study, we have used three types of carbons: Shawinigan carbon black C1 (80 m²/g), high-surface-area carbon C2

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Table 1
Summary of the different samples to study with the variable experimental parameters

Samples	Carbon source	Mixing environment	Mixing method	Atmosphere
THQA21	C1	Dry	Ball-mill	N ₂
THQA22	Graphite	Dry	Ball-mill	N ₂
THQA23	C2	Dry	Ball-mill	N ₂
THQA24	C1	Dry	Ball-mill	Air
THQA25	Graphite	Dry	Ball-mill	Air
THQA26	C2	Dry	Ball-mill	Air
THQA27	Polymer-C1	Acetone	Jar-mill	N ₂
THQA28	Polymer	Acetone	Jar-mill	N ₂
THQA29	Polymer	Water	Jar-mill	N ₂

(2000 m²/g) and natural graphite with 5- μ m particle size (5.6 m²/g). Table 1 summarizes the properties of the different samples and the experimental parameters used in the studies.

The samples were characterized by thermogravimetric analysis TGA (Perkin Thermal Analysis), X-ray diffraction and scanning electron microscopy (SEM). The discharge (intercalation)–charge (deintercalation) cycling of Li₄Ti₅O₁₂ was carried out in 4-cm² laboratory cells (two electrodes) with lithium metal as the counter electrode. The initial cell chemistry is based on the following configuration: Li metal (–)/electrolyte/Li₄Ti₅O₁₂ (+) with a liquid electrolyte (EC/DMC + LiClO₄). The working electrode was prepared from a paste mixture of Li₄Ti₅O₁₂, carbon black for an electronic conductor additive and PVDF binder mixed in NMP. The paste was coated on to aluminum Exmet. The electrode was dried under vacuum at 85 °C for 24 h before electrochemical evaluation. The discharge–charge cycling

and slow potential scan were performed using a constant current method (MacPile^R, Claix, France).

3. Results and discussion

3.1. Solvent effect

The Li₄Ti₅O₁₂ powder is a white insulator when heated in air, however, when heated in N₂ it is clear gray with polymer and dark gray with carbon additive.

The weight losses of the mixed precursors were monitored by TGA. Fig. 1 shows the weight losses of samples THQA27, 28 and 29. The first plateau is associated with polymer carbonization, starting at around 230 °C and finishing at around 510 °C; the weight losses varied from 7, 10 and 13%, respectively, with THQA 27, 28 and 29. The second significant weight loss starts at around 500 °C where the oxidation of carbon initiates a possible reduction of TiO₂ to form TiO. The oxidation of carbon is complete at $T > 670$ °C. The total weight loss is higher when water is used in the process.

XRD analyses indicated that the main phase of the reaction product is Li₄Ti₅O₁₂ with the spinel structure. In general, the absence of the principal peak characteristic of TiO₂ localized at $2\theta = 25^\circ - 24^\circ$ in the product indicates the complete conversion of TiO₂ in the solid-state reaction.

To examine the effect of the mixing method on the structure of Li₄Ti₅O₁₂, XRD analyses were conducted on materials produced by using different mixing environment with polymer as the source of carbon and carbon additive (Fig. 2). The samples obtained by using acetone in the starting

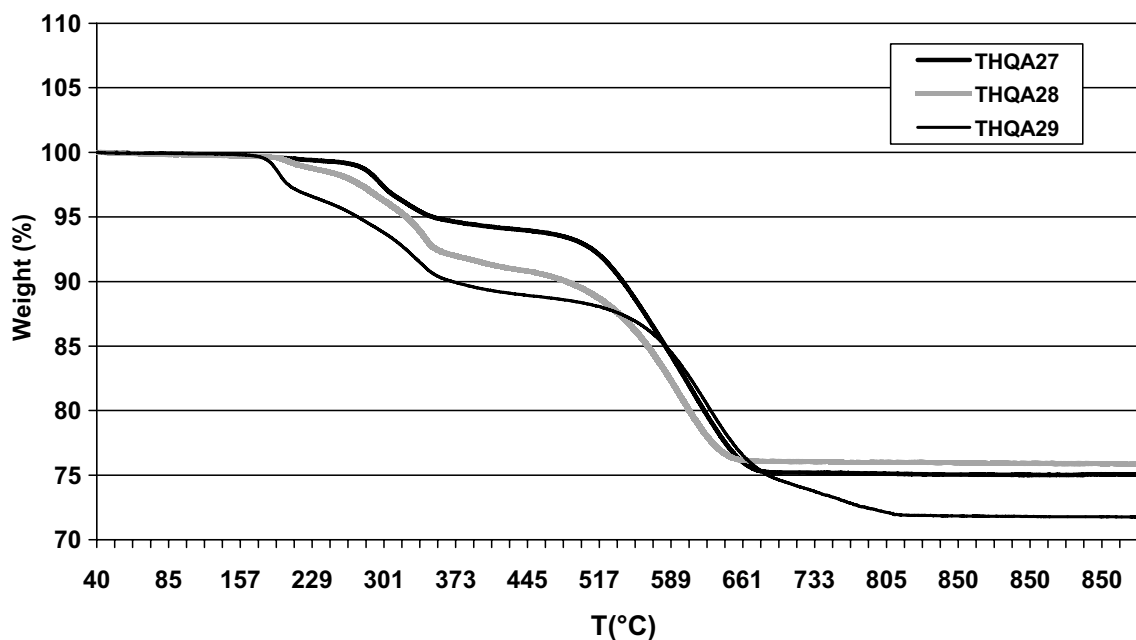


Fig. 1. TGA curves of the weight losses of the mixed precursors before heating.

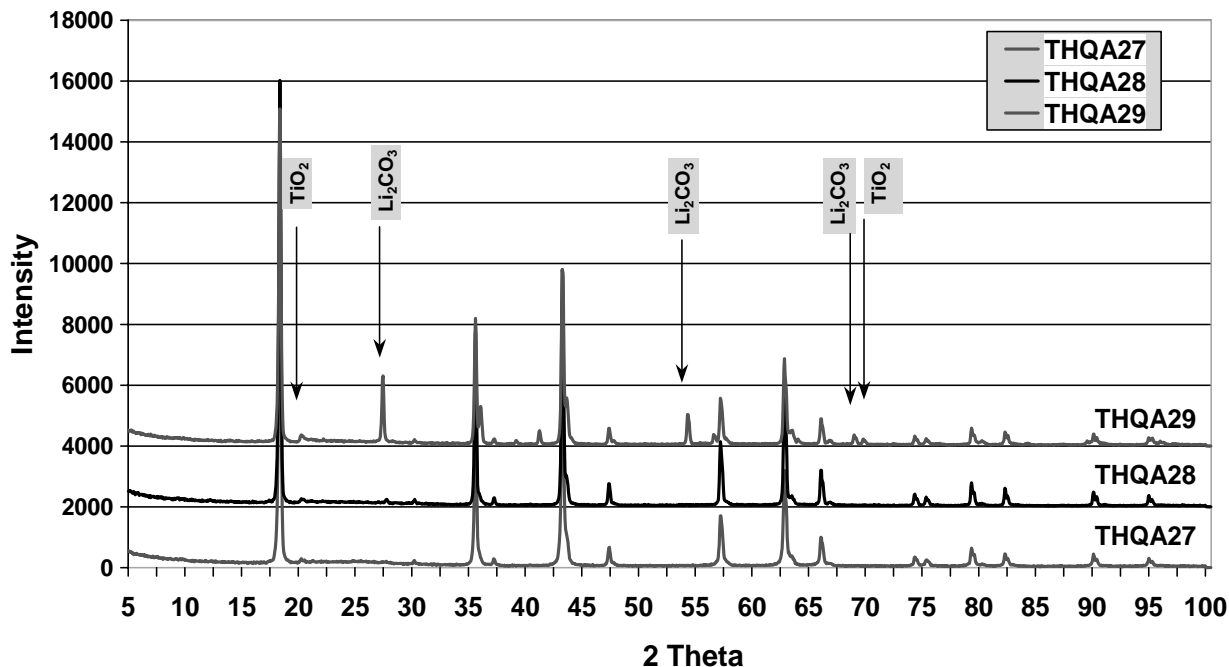


Fig. 2. XRD patterns $\text{Li}_{(4/3+x)}\text{Ti}_{5/3}\text{O}_4$ synthesized at 850°C from wet mixtures in different solvent.

mixture (THQA27, 28) did not show the TiO_2 characteristic peak, while the sample prepared with water (THQA29) showed evidence for a small peak characteristic of TiO_2 and a large XRD peak attributed to Li_2CO_3 . This result suggests that mixtures obtained by using organic solvent produce a pure-material. However, water is not a good medium for forming the mixture because some TiO_2 or Li_2CO_3 was not transformed.

Fig. 3 shows scanning electron micrographs of precursor samples after mixing THQ A27–29 and then after heating

at 850°C in N_2 . Before heating, the polymer coating can be seen on the surface of the particles and the agglomerates. After heating at 80°C , the micrographs reveal that the morphology and particle size were affected by the preparation method. For sample THQA27, having mixed polymer and carbon, two sizes of particles were present, $0.5\ \mu\text{m}$ and less than $50\ \text{nm}$. The fine particles represent residual carbon particles surrounding $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles. However, for the samples containing only polymer, only one type of particle is observed. The particle size of the sample obtained using

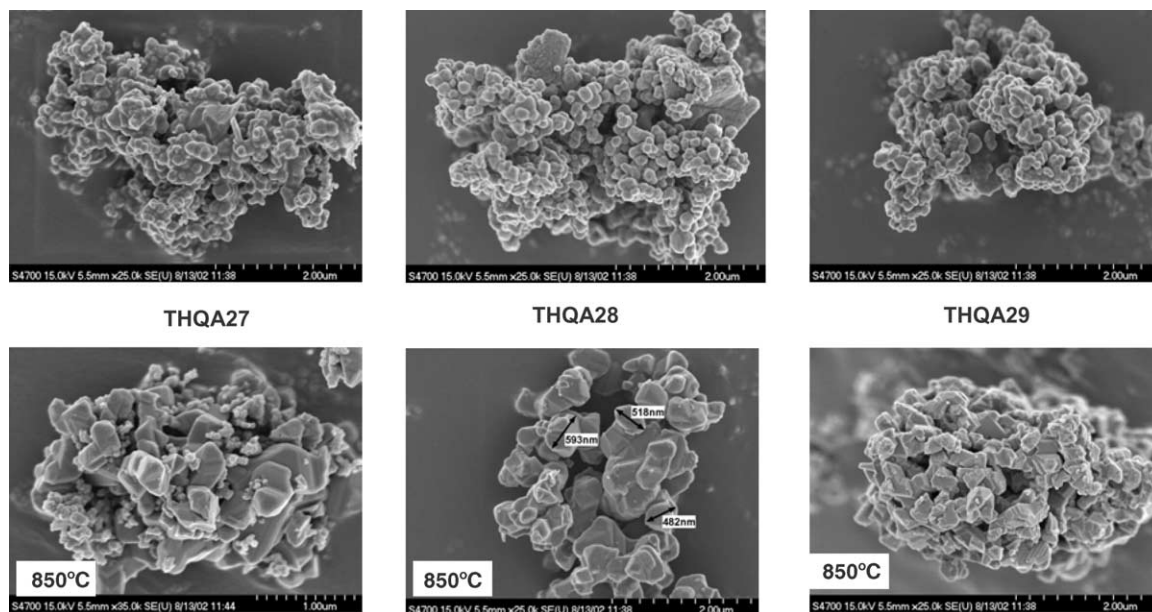


Fig. 3. Scanning electron micrographs of precursor samples after mixing THQ A27–29 and then after heating at 850°C in N_2 .

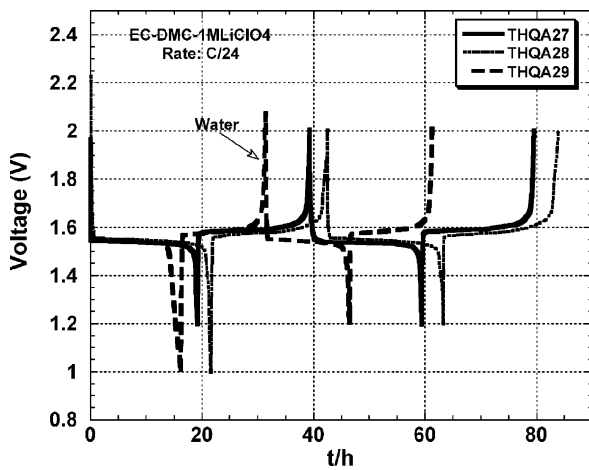


Fig. 4. Discharge–charge curves of the samples THQA27–29 at $C/24$ rate between 1.2 and 2 V.

acetone varies between 0.3 and 0.7 μm , and the particles have a spherical shape. For the sample mixed in water, the particle size varies from 0.15 to 1 μm , and the particles have a lamellar shape.

Fig. 4 shows the discharge–charge curves for the first two cycles of the samples THQA27–29.

The cycles were obtained at the $C/24$ rate between 1.2 and 2 V. Mixing in acetone seems to be a more efficient method to produce very homogenous powders. The reversible capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared in acetone was 147 and 151 mAh/g for samples THQA27 and 28, respectively. On the other hand, a lower capacity of 110 mAh/g was obtained with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared by mixing in water. The reversible capacity and coulombic efficiency are summarized in Table 2.

Table 2

Effect of polymer and mixing solvent on capacity and coulombic efficiency of $\text{Li}_4\text{Ti}_5\text{O}_{12}$

Samples	Carbon source	Rev. cap. (mAh/g) (second cycle)	Coul. eff. (first cycle)
THQA27	Polymer-C1/Acetone	147	101
THQA28	Polymer/Acetone	151	97
THQA29	Polymer/Water	110	94

3.2. Carbon effect

We have used three types of carbons, C1, C2 and graphite mixed with precursors (TiO_2 or Li_2CO_3) in dry process. The heating step was done in N_2 (THQA21–23) or air (THQA24–26). We observed that the morphology of the product $\text{Li}_4\text{Ti}_5\text{O}_{12}$ changes with the type of carbon in the reaction mixture. The SEM images (Fig. 5) shows that different particle shapes are obtained, depending on the carbon precursor used in the synthesis of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. When heated in N_2 , the carbon particles can be visualized as surrounding the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles in all cases. The gas environment was found to affect the shape of particles. As evident in Fig. 4, the particles are more rounded and smaller when air is used in the synthesis.

The results of the electrochemical characterization indicate that the samples heated in N_2 gas show lower reversible capacities and lower coulombic efficiency (Table 3). Fig. 6 shows the discharge–charge curves for the first two cycles with the four samples. The cycles were obtained at the $C/24$ rate between 1.2 and 2 V. A shoulder in the potential profile is present in the discharge curves for samples heated in N_2 . However, no sign of this shoulder is apparent in the profiles

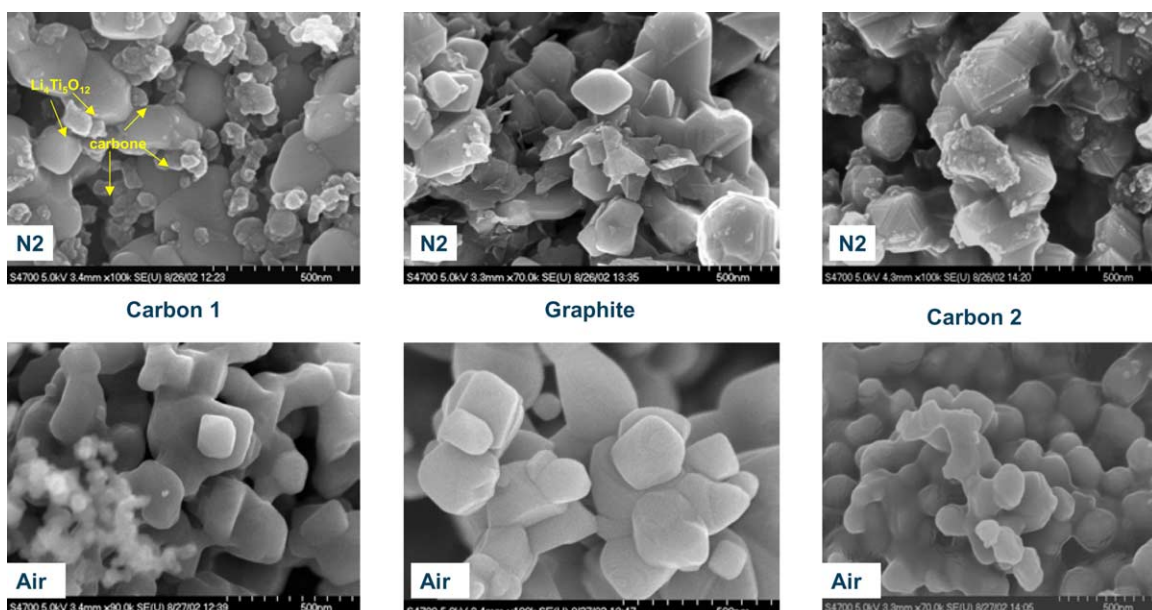


Fig. 5. Scanning electron micrographs samples after mixing THQA21–23 heated in N_2 and THQA24–26 heated in air.

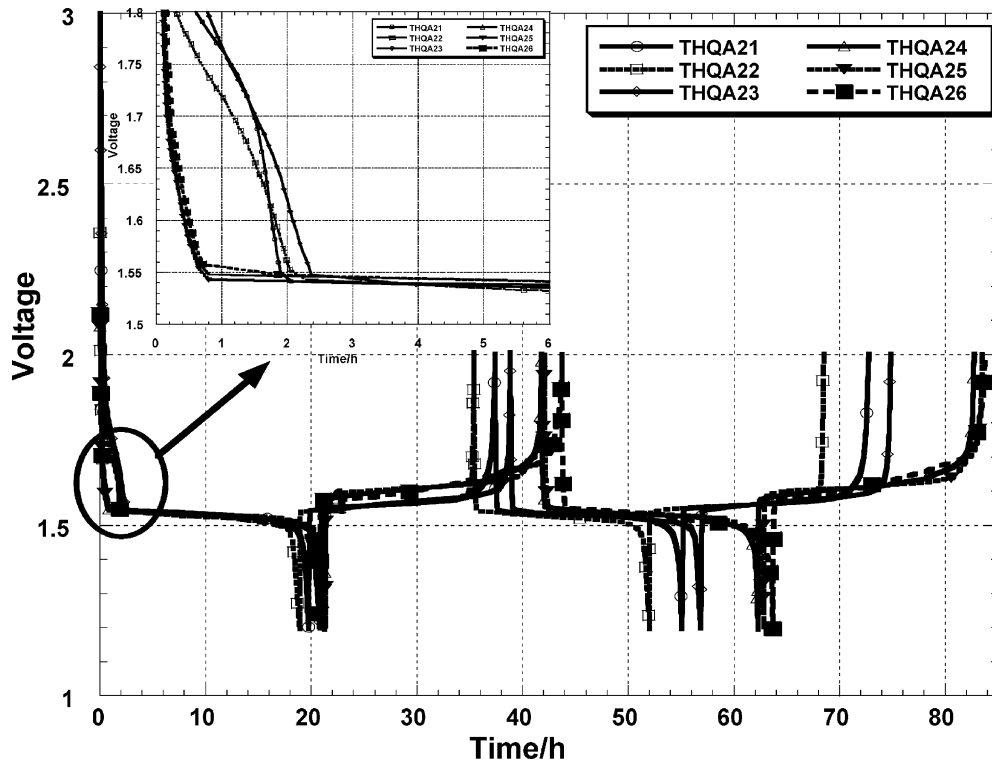


Fig. 6. Discharge–charge curves of the samples THQA21–26 at C/24 rate between 1.2 and 2 V.

of samples heated in air. This result is attributed to catalytic heteroatoms existing on the surface of carbons which impedes the intercalation of Li^+ ions in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ structure. Thus, by using air, the heteroatoms can be eliminated and the capacity increases.

3.3. High rate capability

For evaluation at high rate, we investigated the performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at C/1 between 1.2 and 2 V. Fig. 7 shows the performance at high rate as a function of the precursor and mixing. The dry process shows that higher capacity is obtained. With carbon (C2) as additive, the capacity at C/1 was as high as 144 mAh/g, while the lowest capacity was obtained with graphite. This results can be related to the

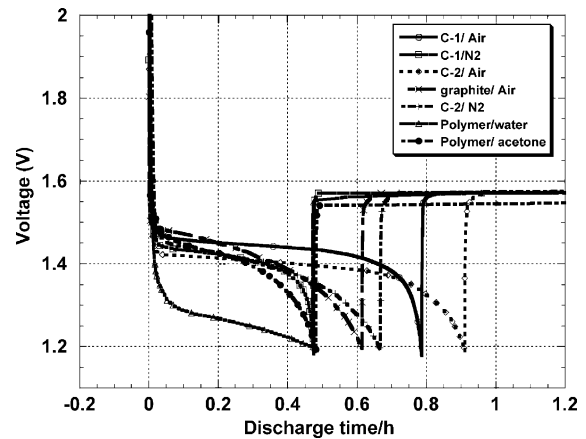


Fig. 7. Performance at high rate as a function of the precursor and mixing.

Table 3
Effect of carbon source on the capacity and columbic efficiency of $\text{Li}_4\text{Ti}_5\text{O}_{12}$

Samples	Carbon source	Rev. cap. (mAh/g) (second cycle)	Coul. eff. (first cycle)
THQA21	C1/N ₂	143	89.8
THQA22	Graphite/N ₂	134	87.6
THQA23	C2/N ₂	146	86.1
THQA24	C1/air	149	96.8
THQA25	Graphite/air	151	97.7
THQA26	C2/air	146	110.5

particle size and the surface area of the carbon used to have uniform mixing [15].

4. Conclusion

Different types of carbons were added to the precursor mixture to synthesize $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Dry mixing was compared to solvent mixing where organic solvents result in better electrochemical performance than obtained with aqueous solvent. The wide variety of particle sizes (from nano to

sub-micron) and shapes obtained, leads us to conclude that the synthesis procedure can be optimized to control the particle size and morphology.

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