Li₄Ti₅O₁₂ thin-film electrodes by in-situ synthesis of lithium alkoxide for Li-ion microbatteries

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Abstract

Rechargeable thin-film batteries have recently become the topic of widespread research for use as efficient energy storage devices. Spinel Li₄Ti₅O₁₂ has been considered as one of the most prospective anode materials for Li-ion batteries because of its excellent reversibility and long cycle life. We report here the sol-gel synthesis and coating preparation of spinel thin-film Li₄Ti₅O₁₂ electrodes for Li-ion microbatteries using lithium ethoxide produced *in situ* that reacts with titanium alkoxide to produce the precursor solution without particle precipitation. This synthesis procedure reduces the thermal treatment to obtain a pure phase at only 700 °C and 15 minutes. The physical and structural characterization of the 300 nm Li₄Ti₅O₁₂ coatings shows a very homogeneous distribution of elements and a pure spinel phase. Galvanostatic discharge-charge tests indicate maximum discharge capacities of 152 mA h g⁻¹ when the material is treated at 700 °C for 15 minutes.

Keywords: Li-ion microbatteries, Sol-Gel, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Nanocrystalline materials, Thin film, Coatings

1. Introduction

Rechargeable thin-film batteries have recently become the topic of widespread research for use as efficient energy storage devices in many lightweight electronic appliances, cellular phones and laptop computers, because of the high energy densities. There have been many efforts to make microscale lithium batteries for various application fields related to microsystems, such as microsensors, micromechanics, and microelectronics [1-6]. The general requirements of the microbatteries for these applications are high specific energy, wide range of temperature stability, low self discharge rate and flexibility of cell design [7]. Thin-film Li-ion batteries fabricated using only solid-state materials, including the electrolyte, by a thin-film process is very beneficial because of its excellent safety and good rechargeability and is expected to fulfill the requirements above [8].

Among the different electrodes used, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been considered as one of the most prospective anode materials for Li-ion batteries because of its excellent reversibility and long cycle life. It has an excellent Li ion mobility and exhibits almost no structural change (zero-strain insertion material) during charge–discharge cycling [9–13]. Li-ion intercalation in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ occurs via a two-phase coexistence process, resulting in a very stable discharge voltage at around 1.55 V (vs. Li/Li^+). During the discharging process, a maximum theoretical gravimetric capacity of 175 mA h g^{-1} can be reached. The lattice parameter for a spinel unit cell $(\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4)_8$ is $8.36 \text{ \AA}$ [7,14].

Sol-gel route synthesis is a general and effective method for the preparation of micro/nanostructured materials with well controlled morphology and structure. The synthesis of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ using the sol-gel method has been mainly focused on the preparation of particles with optimized properties to improve electrochemical performance as particle size, doping with other elements, porosity, etc. In this case, a titanium alkoxide is usually used in combination with lithium salts as lithium carbonate [15], lithium acetate [16-18] or lithium nitrate [19]. Only several publications have been devoted to the preparation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coatings using the sol-gel method, and most of them use lithium salts as precursors [20-23]. Our previous work in this area studied the preparation of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin-films by dipping using lithium acetate and titanium isopropoxide as main precursors [24,25]. An analysis of the different processing parameters on the electrochemical behavior and a deep structural characterization was also performed. The problems associated with mixing salts and alkoxides precursors is the different hydrolysis and condensation reactions rates, leading to long thermal treatments to produce the pure spinel phase.

In this context, the solution methods using only alkoxide precursors show promising potential for control over particle size, high purity, good chemical homogeneity, low thermal treatments temperatures and times, and micro-structural uniformity. When compared to micro-crystalline ceramics, the different but often desirable behaviour of nano-scaled materials is attributed to the large amount of atoms located in the grain boundaries of the tiny crystallites. Despite the versatility of alkoxide based sol-gel synthesis, its application is rather limited mainly due to the commercial unavailability of suitable precursors especially for mixed-metal oxides. The sol-gel synthesis of binary oxides is usually carried out using a mixture of alkoxides as precursors, however, this approach suffers from the different hydrolysis susceptibilities of the individual

components and the benefits of improved homogeneity can be lost during the hydrolysis of mixtures of alkoxides which may ultimately lead to component segregation, mixed phases or non-ideal stoichiometry in the final ceramic material [26]. The synthesis of double metal alkoxides containing lithium can be produced through a condensation reaction with elimination of a volatile side product. The simplest of these is the reaction of metallic lithium with an alkoxide in a solution of either pure alcohol or alcohol and some organic solvent. This reaction results in the formation of a double metal alkoxide and evolution of hydrogen gas [27]. A bimetallic precursor has the potential to control stoichiometry at the molecular level and thus make this critical parameter less sensitive to processing conditions. In the case of sol-gel processing, hydrolysis steps proceed via intermediates which would ideally retain the original metal stoichiometry. One concern is that hydrolysis of a heterometallic alkoxide containing metals with very different metal hydroxide/oxide solubilities might undergo metal "segregation" with rapid precipitation of only one of the hydrous metal oxides [28,29]. On the other hand, the formation of a thermodynamically favoured heterometal alkoxide assembly is subject to various factors such as the atomic size of the metallic elements and steric bulk of the alkoxo ligands and the synthesis of a heterometal precursor with targeted ratio of metallic elements cannot be achieved by simply mixing the two or more components in required molar ratios. The metal stoichiometry in the isolated product is thus often inappropriate for the material science requirements. The appropriate metal ratio is of prime consideration in assessing the feasibility of heterometal alkoxides as precursors to useful multi-component metal oxides [30].

L. Kavan and M. Grätzel [31] prepared nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles in a slurry using lithium ethoxide and Ti (IV) alkoxides. The incorporation of Polyethylene glycol produced a viscous liquid that was deposited using a doctor-blading technique. The

thickness is about 2 – 4 μm and the electrochemical performance is excellent, at least at the beginning of the charging/discharging cycling. Based on these previous studies, here we report for the first time the sol–gel synthesis and coating preparation of spinel thin-film $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes for Li-ion microbatteries using lithium ethoxide produced *in situ* that reacts with titanium alkoxide to produce the precursor solution without particle precipitation. The hypothetical formation of the double Li-Ti alkoxide results in a drastic reduction of the heat treatment (only 15 minutes) necessary to obtain the pure phase.

2. Experimental

The solution (atomic ratio Li/Ti = 1/1) was prepared using titanium isopropoxide (ABCR, 97%) and lithium (Aldrich, 99.9 %) as precursors, absolute ethanol (Panreac) and acetic acid (Merck, 100%). Final molar ratios of Li:Ti:ethanol:acetic acid were 1:1:16:4.8. The commercial absolute ethanol was distilled to eliminate impurities and then drying using molecular sieves (0.4 nm – pellets, 1.6 mm diameter) from Sigma-Aldrich. Lithium was first slowly dissolved in distilled ethanol inside a bath with ethanol previously cooled at $-16\text{ }^{\circ}\text{C}$, so that sol temperature does not exceed $26\text{ }^{\circ}\text{C}$. After all the lithium pieces have been dissolved and ethanol bath is retired, the resulting solution is clear and colorless. After this, titanium alkoxide was slowly incorporated by stirring at room temperature for sixteen hours. Finally, acetic acid was added to promote sol–gel hydrolysis and condensation reactions by stirring at room temperature for two hours. All the procedure was performed in an Ar atmosphere inside a glove box with water content below 5 ppm.

Quartz substrates were used to assess the homogeneity of the coating and thickness measurement; silicon substrates for structural characterization and gold-coated quartz substrates, prepared by sputtering, for electrochemical characterization. The coatings were prepared by dipping the different substrates using a withdrawal rate of around 19 cm min^{-1} . Thermal treatments were carried out directly at 500, 600 and 700°C for 15 minutes in an Argon atmosphere to sinter the coatings and obtain the adequate crystalline structure. The weight of the coatings was measured using a microbalance (XP26, METTLER TOLEDO) that offer a capacity of 22 g with 0.001 mg readability.

Spectral Ellipsometric measurements were performed using a Variable Angle Spectroscopic Ellipsometer (WVASE32, M-2000UTM, J.A. Co., Woollam) to characterize thickness (e) of films deposited on quartz substrates. The spectra were taken in the visible region, between 250 and 900 nm at a variable incident angle of 65, 70 and 75° . The data were fitted using the WVASE32 software and taking into account a Cauchy model. Characterization of the coatings also includes analysis of a cross-section of coated samples performed by scanning electron microscopy (SEM-JEOL, JSM-6610A), equipped with an energy dispersive X-ray spectroscopy system (EDX, JED-2300, JEOL). The crystal structure of the coated samples was characterized by Grazing incidence X-ray diffraction (step: 0.040° and angle: 0.5°) using a Siemens D-5000.

A JEOL TEM 2010 (200 kV) transmission electron microscope (TEM) equipped with a Gatan CDD camera was used to characterize the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ films, to evaluate the particle size and the crystal structure of the films. Samples were prepared by scratching the films; and wet-grinding of the scratched films is then performed. A drop of the solution is deposited onto holey-carbon film supports. Multiple areas of around $100 \text{ }\mu\text{m} \times 100$

μm were examined for each sample to ensure that the images are representative of the thin films.

FTIR spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer in the range $4000 - 400 \text{ cm}^{-1}$ in transmittance mode with a resolution of 4 cm^{-1} onto coated silicon substrates. Raman study was carried out using a Confocal Micro-Raman (Witec alpha-300R) with laser excitation of 532 nm and a 100x objective lens ($\text{NA}=0.9$) for coatings deposited on Au/Quartz substrates. The optical resolution diffraction of the Confocal Microscope is limited to 200 nm laterally and 500 nm vertically, and Raman spectral resolution of the system is down to 0.02 cm^{-1} .

Compositional depth profiling of the spinel coated quartz substrates treated at 500, 600 and 700°C for 15 minutes were obtained using a TOF-SIMS⁵ spectrometer (Ion ToF). A pulsed 25 kV Bi^+ primary ion source was employed for analysis, delivering 1.2 pA of target current over a $21.9 \mu\text{m} \times 21.9 \mu\text{m}$ area. Sputtering was done using a 2 kV Oxygen beam over a $250 \mu\text{m} \times 250 \mu\text{m}$ area. Data acquisition and post-processing analyses were performed using the Ion-Spec software.

Electrochemical behavior of the films prepared on Au/Quartz substrates was carried out in an argon filled three-electrode beaker cell using two Li foils as the counter and reference electrodes, and 1M LiPF_6 / (EC-DEC) as liquid electrolyte. The three components, lithium foils and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film, were immersed in this electrolyte. Cyclic voltammetry and galvanostatic charge/discharge measurements (Multichannel Potentiostat VMP3 from Biologic) were conducted on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ films using cutoff voltages at 2.0 and 1.2 V versus Li/Li^+ . Cycling was performed by series of 20 cycles at different current intensities corresponding to C/2, 1 C, 2 C, 4 C and 8 C.

3. Results and discussion

The sol is transparent without the presence of phase separation or precipitates that leads to homogeneous and transparent coatings on the three substrates after all thermal treatments. Spectral ellipsometry measurements indicate average thickness of coatings around 310 nm for the three thermal treatments. The cross-section SEM micrographs of a coated sample treated at 700 °C for 15 minutes (Fig. 1) presents a dense, homogeneous and well-bonded layer. The micrograph obtained at higher magnification shows an outer layer (spinel coating) comprised of small aggregates. The thickness of the spinel coating from this figure is around 330 nm, in accordance with ellipsometry results considering the surface irregularities. The gold layer, prepared by sputtering on quartz substrates, can be observed between the substrate and the spinel coating with a thickness of about 120 nm.

Fig. 2 shows the grazing incidence X-ray of coatings treated at 500, 600 and 700 °C. The three treatments only present the peaks associated with the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel phase (JCPDS # 49-0207), although a small peak could be detected at around 25 degrees. This small peak would be associated with a very low amount of Anatase (TiO_2) (JCPDS # 21-1272), as a secondary phase. This is a remarkable result considering the short duration of the thermal treatments, 15 minutes. The results clearly show the importance of the thermal treatment temperature, because the degree of crystallinity increases considerably with increasing temperature. The calculated lattice parameter a is 8.357, 8.358 and 8.359 Å for coatings heat-treated at 500, 600 and 700 °C for 15 minutes, respectively, which is in good agreement with the theoretical value of 8.358 Å for the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel phase (JCPDS # 49-0207). Figure 3 shows the high-resolution TEM images of a scratched $\text{Li}_4\text{Ti}_5\text{O}_{12}$ film after thermal treatment at 700°C. The image a) shows a surface area with a high homogeneity and uniform crystalline

particles of 20 nm in size. From the image b), the clear lattice fringes of the thin films with an interplanar distance of 0.48 nm can be seen, corresponding to the d-spacing of the (111) crystal plane. This provides further evidence of the highly crystallized spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase.

The presence of a pure phase is confirmed by FTIR spectra scanned in the wavenumbers range from 1850 to 400 cm^{-1} (Fig. 4). The film heat-treated at 500°C shows a different spectra that samples treated at higher temperatures mainly due to the lower inorganic condensation. For this thermal treatment, it is possible to observe bands related to lateral chains of the alkoxide and residual reaction products such as stretching vibration mode of $\nu(\text{C}=\text{O})$ from $-\text{CO}_2$ at 1582 cm^{-1} which may be the decomposition product of lateral chains combined with oxygen from $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [32]. Bending modes of methyl and ethyl groups around 1435 cm^{-1} and the appearance of two other peaks at 1214 and 1052 cm^{-1} , which are due to stretching modes $\nu(\text{C}-\text{O}-\text{C})$ and $\nu(\text{O}-\text{C}-\text{C})$, respectively, confirm the presence of an ester [33]. On the other hand, it is possible to observe, for samples treated at higher temperatures, a broad peak centered at 1110 cm^{-1} that involves both, a stretching vibration band of $\text{Si}-\text{O}-\text{Si}$ and a shoulder at 1040 cm^{-1} assigned to $\text{Li}-\text{O}-\text{Si}$ from the substrate. The band at 963 cm^{-1} is assigned to $\text{Ti}-\text{O}-\text{Ti}$ frequency [33-35]. Two broad absorption bands centered at 646 and 455 cm^{-1} are due to the symmetric and asymmetric stretching vibrations of the octahedral groups of TiO_6 , respectively, typical coordination of normal spinel. Also it is possible to see a band at 515 cm^{-1} related to Ti^{4+} in a tetrahedral coordination, suggesting some degree of inversion in the spinel structure, which disappeared with increasing heat treatment [36,37]. Bands at 646, 606, 560 and 440 cm^{-1} are observed for samples heat-treated at 600°C and 700°C and are related to $\text{Ti}-\text{O}$ hexacoordinated bonds (TiO_6). The bands at 646, 606 and 560 cm^{-1} are assigned to the stretching modes of TiO_6 and the band at 440 cm^{-1} was assigned to

bending mode [38]. In conclusion, The FTIR analysis indicates the persistence of organic groups and a limited formation of spinel structure for samples treated at 500 °C in comparison with samples treated at 600 and 700 °C for 15 minutes.

Raman spectroscopy is an effective structural tool capable of discriminating or “fingerprinting” different local bonding configurations; it is often superior to infrared spectroscopy for investigating inorganic systems because the vibration energies of metal-ligand bonds are generally in the range from 100 to 700 cm^{-1} , a region of the infrared spectrum that is experimentally difficult to study. The Raman spectrum of nanocrystalline $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (Figure 5) shows the characteristic allowed lines at 225, 272, 340, 420, 514 and 675 cm^{-1} . All of these peaks, except for the ones at 272 and 340 cm^{-1} , show overall broadening lines. Sample heat-treated at 500°C only present the most intense lines located at 235, 430, and 675 cm^{-1} . In lithium titanate, frequencies in the 700-550 cm^{-1} region are assigned to Ti-O stretches in TiO_6 octahedra [39]. The higher frequency band at 675 cm^{-1} was assigned to vibrations of Ti–O stretching vibrations in TiO_6 octahedra whereas the 420 and 340 cm^{-1} Raman lines were assigned to the stretching vibrations of the Li-O bonds in LiO_4 and LiO_6 polyhedra, respectively [40-42]. The Raman bands below 300 cm^{-1} were attributed to the bending vibrations of O-Li-O bonds (225 cm^{-1}) and O-Ti-O bonds (272 cm^{-1}) [43,44]. Julien et al. [40] reported also the Raman spectra of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ that was found to display bands at 671, 430, 347, 271, and 232 cm^{-1} which were tentatively assigned to the five expected A_{1g} , F_{2g} , and E_g symmetry species for the spinel Oh 7 spectroscopic point symmetry group.

The Li_2TiO_3 phase usually shows bands at 355 cm^{-1} (Li–O stretching vibrations in LiO_6 octahedra), 422 cm^{-1} (Li–O stretching vibrations in LiO_4 octahedra) and 663 cm^{-1} (Ti–O stretching vibrations in TiO_6 octahedra) [45,46]. It seems that Raman spectra confirm the absence of this phase in the films. Also, no peaks from anatase (144 cm^{-1} , E_g) or

rutile (610 cm^{-1}) phases are observed in Figure 5, indicating the purity of the spinel phase.

Fig. 6 shows the TOF-SIMS depth profiles of the coatings on quartz treated for 15 minutes at different temperatures as obtained from the corresponding secondary ions. A homogeneous elements distribution can be observed for the coatings treated at all temperatures. The location of the lithium titanium oxide layer / quartz substrate interface can be approximately determined by the intersection of the corresponding lines. This position is situated at a slightly higher sputtering time in the case of the sample treated at $600\text{ }^{\circ}\text{C}$ for 15 minutes. It is possible that this coating is a little thicker in the tested area because of the influence of different parameters as surface irregularities, withdrawal rate, temperature inside glove box, etc.

The electrochemical properties of the films were evaluated using cyclic voltammogram at 3 mV/min (not showed). As a typical result, only one anodic and one cathodic sharp peaks can be observed, indicating that the film is simple phase of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The pair of redox reaction peaks, located between 1.5 and 1.6 V , is characteristic of electrochemical lithium insertion/extraction of this spinel phase [47]. Fig. 7a displays the sixth galvanostatic discharge-charge profiles of the spinel electrode heat-treated at $600\text{ }^{\circ}\text{C}$ for 15 minutes at different current rates corresponding to $C/2$, 1 C , 2 C , 4 C and 8 C . We note that 1 C is defined as the intercalation of 3 Li^+ per formula unit in 1 h at $25\text{ }^{\circ}\text{C}$. The cell was discharged to 1.2 V , and then charged and discharged between 2.0 V and 1.2 V . In the charge/discharge processes, typical plateau at around 1.55 V (vs. Li^+/Li) was observed, which is in agreement with the potentials showed in the cyclic voltammogram, and characteristic of a capacitive discharge. All the curves exhibit an abrupt drop in voltage at the beginning of discharge (Li^+ intercalation), and the charge and discharge curves do not form a very flat plateau, a consequence of the lower

crystallinity obtained after this short thermal treatment at 600 °C. As the current rate increased, the charge and discharge capacities gradually decreased. The discharge capacity dropped with increasing discharge rate from 75 mA h g⁻¹ at the C/2 rate to 21 mA h g⁻¹ at the 8C rate.

The behavior observed with the coating heat-treated at 700 °C for 15 minutes at different current rates corresponding to C/2, 1 C, 2 C, 4 C and 8 C (Fig. 7b) is quite different. Again, the typical plateau at around 1.55 V (vs. Li⁺/Li) is observed in the charge/discharge processes, but in this case this plateau is very flat indicating a well developed crystalline structure as X-Ray diffraction pattern confirmed. The discharge capacity at C/2 rate is high (152 mA h g⁻¹) and close to the theoretical capacity. The increase of current rate leads to a common reduction of capacity with values of 138, 129, 121 and 111 mA h g⁻¹ for 1 C, 2 C, 4 C and 8 C rates. Compared with the sample treated at 600 °C, the electrode treated at 700 °C shows a lower reduction of capacity when the current rate increases, confirming a better conformation of the spinel structure that allows a faster diffusion of lithium ions.

Fig. 8 shows the discharge and charge capacities vs. cycle number of spinel electrodes treated at 600 and 700 °C (15 minutes) for different C rates: C/2, 1 C, 2 C, 4 C and 8 C. Irreversible capacity was observed during the first cycles for both kinds of samples. The reason for this behavior is not clear, but may be due to the growth of a surface layer on the film surface [47]. As the discharge current rate increases, the capacities gradually decreased. Again it is possible to see that the thermal treatment at 700 °C has been more efficient to produce a well crystallized spinel structure and higher capacities are obtained.

Fig. 9 presents a cross-section SEM micrograph of a coated sample treated at 700 °C for 15 minutes after the galvanostatic cycling to determine whether structural changes occur upon lithiation. Despite cycling, the figure provides evidence that galvanostatic cycling does not lead to the appearance of cracks at the micrometer level, which helps to explain both the cycling stability and rate capability of these thin film materials. The main change in comparison with the coating before cycling is the presence of a greater amount of residual porosity resulting from the penetration of the liquid electrolyte in the material.

4. Conclusions

The new synthesis procedure of thin-film $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coatings for electrodes based on the in-situ production of a lithium alkoxide and its reaction with a titanium alkoxide reduces the thermal treatment to obtain a pure phase at only 700 °C and 15 minutes. The physical and structural characterization of the 300 nm $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coatings shows a very homogeneous distribution of elements and a pure spinel phase. Galvanostatic discharge-charge tests indicate maximum discharge capacities of 152 mA h g^{-1} when the material is treated at 700 °C for 15 minutes.

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Figure captions

Fig. 1. Cross-section SEM micrographs (different magnifications) of a coated sample treated at 700 °C for 15 minutes before galvanostatic cycling.

Fig. 2. Grazing incidence X-ray of coatings treated at 500, 600 and 700 °C for 15 minutes.

Fig. 3. a) HR-TEM micrograph of powder scratched from a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin-film heat-treated at 700°C. b) Magnified image of a) revealing the (111) plane of $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Fig. 4. FT-IR spectra of coatings treated at 500, 600 and 700 °C for 15 minutes.

Fig. 5. Raman spectra of coatings treated at 500, 600 and 700 °C for 15 minutes.

Fig. 6. TOF-SIMS depth profiles of the coatings on quartz treated for 15 minutes at a) 500°C, b) 600 °C and c) 700 °C.

Fig. 7. Sixth galvanostatic discharge-charge profiles of the spinel electrode heat-treated at a) 600 °C and b) 700 °C for 15 minutes at different current rates corresponding to C/2, 1 C, 2 C, 4 C and 8 C.

Fig. 8. Discharge and charge capacities vs. cycle number of spinel electrodes treated at a) 600 and b) 700 °C (15 minutes) for different C rates: C/2, 1 C, 2 C, 4 C and 8 C.

Fig. 9. Cross-section SEM micrograph of a one-layer coated sample treated at 700 °C for 15 minutes after galvanostatic cycling.

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