TiO₂–POLYMER NANO–COMPOSITES BY SOL–GEL

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Sol-gel processes make it possible to develop new hybrid electrolyte materials of the type ceramic-polymer, known as Nano-Crystallite-Insertion-Material (NCIM). They can be used in reversible alkali electrochemical cells after insertion with cations such as Li⁺. In the present study, TiO₂-polyethylene oxide hybrid materials were synthesized from TiCl₄ and from Ti ethoxide. Their structure is analyzed in relation with the processing parameters. A primary evaluation of the nanoscale composite materials for reversible Li insertion was performed.

1. INTRODUCTION

Recently, the investigation of new organic-mineral hybrid copolymers was undertaken for possible applications as battery electrodes and electrochrome devices. For instance, complexes such as (PEO)₈SnCl₄ or (PEO)₈SnCl₄·4H₂O, where (PEO) stands for polyethylene oxide, were prepared [1]. Other hybrid materials made from the same chemical components include nanocomposites comprised of fine SnO₂ grains made by sol-gel, embedded in a PEO matrix [2]. More recently, the development of TiO₂ nanoscale insertion composite materials were proposed [3]. These nanoscale grains provide many broken bonds on the surface where reversible alkali adsorption could be achieved.

In the present study, we focused on the fabrication of such hybrid materials with the TiO₂ nanoscale phase, by controlled hydrolysis of mixed solutions of metal and polymer precursors. The polymer chemical precursor was PEO, while 2 ceramic precursors were investigated; TiCl₄ and the ethoxide Ti(OC₂H₅)₄. The fabrication and structure of these materials is presented.

2. EXPERIMENTAL

The chemical products used in this investigation were from Aldrich. The PEO, in which EO stands for —CH₂CH₂O— and P for “poly,” had an average molar mass of 100,000. The Ti(OC₂H₅)₄ was a 20% solution of technical grade ethoxide

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in ethanol. The TiCl_4 was 99.9% pure. It was a liquid with the aspect of water kept under nitrogen in a sure-seal bottle. This product reacts very violently with any trace of water and produces a HCl gas. It was always transferred under nitrogen with needles, in the present study.

Some polymer reference samples were only made by hydrolysis of PEO without any TiO_2 . Similarly, some TiO_2 reference samples were only made by hydrolysis of each Ti precursor. Then, a range of $(\text{PEO})_n\text{TiO}_2$ hybrid materials with $n = 4$ to 16 were synthesized with each Ti precursor. Two different dry solvents were used: acetonitrile and pentanol. The effects of slow hydrolysis by air humidity and fast hydrolysis in excess water were compared. The structures of synthesized hybrids were analyzed up to 600°C by powder X-ray diffraction, and scanning electron microscopy (SEM). Preliminary Li insertion was carried out on one material.

3. RESULTS

The reference TiO_2 samples made at 20°C from TiCl_4 or from $\text{Ti}(\text{OC}_2\text{H}_5)_4$ by hydrolysis with an excess of water or by the air humidity were all amorphous (Fig. 1a). They crystallized to anatase form at 180°C (Fig. 2d). As for PEO, it showed the crystalline X-ray diffraction data in Fig. 1e, both for the initial power or when drying to a strong polymer film. The hybrid $(\text{PEO})_n\text{TiCl}_4$ materials made were the same in dry pentanol or in dry acetonitrile, for a given set of precursor content and hydrolysis conditions. When hydrolyzed by air humidity, they were X-ray amorphous for $n = 4$ (Fig. 1b). For $n = 8$, the X-ray structure was a mixture of amorphous TiO_2 and crystalline PEO (Fig. 1c). For $n = 16$, the amorphous spectrum of TiO_2 was no longer observed (Fig. 1d). However, while the hydrolysis of mixed $(\text{PEO})_8\text{TiCl}_4$ solutions by air humidity led to a crystalline PEO phase (Fig. 1c and Fig. 2a), hydrolysis of the same solutions by excess water led to completely X-ray amorphous hybrid materials (Fig. 2b).

SEM observations of all samples hydrolyzed by air humidity actually showed the presence of 2 phases, even in the X-ray amorphous $(\text{PEO})_4\text{TiCl}_4$ material. Each phase was separated in macroscopic domains several $100\ \mu\text{m}$ in extent. One phase had the aspect of PEO while the second phase was a very viscous brown gel that did not dry at 20°C . The viscous gel could be dried with difficulty under vacuum at 65°C and it gave gel fibers with a high TiO_2 content and some residual chlorine, according to qualitative EDX analysis. For $n = 4$, both phases were rather featureless, while for $n = 16$ the extensive planar agglomeration of PEO crystallites formed during drying could be observed. The aspects of both phases for $n = 8$ can be seen in Fig. 3a. The only homogeneous samples according to SEM observations (Fig. 3b) and with an amorphous X-ray diagram (Fig. 2b), were made by hydrolysis in excess water of mixed $(\text{PEO})_8\text{TiCl}_4$ solutions.

By comparison with TiCl_4 , all $(\text{PEO})_n\text{Ti}$ materials made from mixed PEO and $\text{Ti}(\text{OC}_2\text{H}_5)_4$ solutions, and hydrolyzed by air humidity or by excess water, showed the X-ray pattern of crystalline PEO as in Fig. 1c or Fig. 1d. In all samples hydrolyzed by air humidity, the 2 phases were easily distinguished under the SEM. A thin layer of TiO_2 gel segregated and formed on top of the PEO (Fig. 3c). In Fig. 3c, the PEO appears to be above because the dried samples was observed

FIGURE 1 X-Ray diffraction spectra of hybrid $(\text{PEO})_n\text{TiCl}_4$ material made by hydrolysis by air humidity in dry pentanol. The Spectra of PEO and of TiO_2 from TiCl_4 obtained in the same conditions are also reported.

from below. An EDX analysis confirmed the fibers mostly consisted of a TiO_2 gel, while the particles linked by the gel were mostly PEO. On the contrary, in the $(\text{PEO})_8\text{Ti}$ sample hydrolyzed by excess water, phase separation occurred on a uniform nanoscale, making a uniform composite throughout the sample (Fig. 3d). The TiO_2 phase consisted of submicron fibers (Fig. 4) linking an open packing with uniform porosity of PEO flakes.

TGA analysis showed that the polymer phase in all hybrid materials was progressively destroyed from 200 to 350°C . Then the TiO_2 crystallized in the anatase form as shown in Fig. 2c for amorphous $(\text{PEO})_8\text{TiCl}_4$ sample hydrolyzed in excess water after heat treatment at 550°C (Fig. 2c). Li insertion is now being studied in this last sample, and preliminary results showed that such an insertion is

FIGURE 2 X-ray diffraction spectra of $(\text{PEO})_8\text{TiCl}_4$ hybrids made by hydrides of mixed pentanol solution: (a) by air humidity at 20°C ; (b) by excess water at 20°C ; (c) by excess water, after heat treatment at 550°C ; in (d) TiO_2 made in excess water at 20°C from TiCl_4 , then crystallized at 180°C . (e) by excess water after insertion of Li and heat treatment at 550°C .

reversible. The Li insertion composite gives a $\text{Li}_{2.0}\text{TiO}_2$ compound by heat treatment at 550°C (Fig. 2e).

4. DISCUSSION

PEO is known to be an excellent host material for a number of salts, and a detailed review of their structures and properties was provided by Ratner and Shriver [4]. These materials are good ionic conductors above their glass transition T_g , due to a molten micro-environment where the ions can move by a local liquid-like process. They can be mostly made with monovalent cations such as Na^+ , Li^+K^+ , and Ag^+ . The backbone oxygen of EO act as Lewis-base sites to complex the alkali. The cations are strongly solvated by these oxygen. These materials also

FIGURE 3 SEM micrographs of $(\text{PEO})_8\text{TiCl}_4$ samples in dry pentanol by hydrolysis at 20°C : (a) by air humidity; (b) by excess water. $(\text{PEO})_8\text{Ti}$ samples made from $\text{Ti}(\text{OC}_2\text{H}_4)_4$ at 20°C in dry pentanol, hydrolyzed: (c) by air humidity; (d) by excess water.

FIGURE 4 SEM micrographs of the $(\text{PEO})_8\text{Ti}$ samples in Fig. 3d, made from $\text{Ti}(\text{OC}_2\text{H}_5)_4$ at 20°C in dry pentanol, hydrolyzed by excess water.

show complex phase diagrams [5]. At high temperature, a single elastomeric liquid or amorphous phase with high conductivity is present. At lower temperatures, 2 phases are usually present, which can be a liquid and a polymer. Obviously, all of our $(\text{PEO})_n\text{TiCl}_4$ and $n \geq 8$ showed this mixture liquid + PEO-like structure. The liquid led to a TiO_2 gel type phase.

The hybrid materials synthesized in this study can be divided in 3 categories. A first category with homogeneous SEM and X-ray aspects only comprised the $(\text{PEO})_8\text{TiCl}_4$ material made by simultaneous hydrolysis of PEO and TiCl_4 in excess water. This is consistent with the fact that all the precursors in this study undertake fast hydrolysis, and that hydrolysis occurred in many nucleation centers in excess water. Hence, this material was either homogeneous on an atomic scale, or heterogeneous on a scale well below a micrometer. Actually, the formation of anatase in all samples near 400°C , including this sample, indicates that we always had 2 phases. In the $(\text{PEO})_8\text{TiCl}_4$ sample hydrolyzed in excess water, the heterogeneity was too fine to be observed under the SEM.

This view is confronted by the structure of samples made from Ti-ethoxide hydrolyzed in excess water, by comparison with the same samples hydrolyzed by air humidity. Both samples belong to the same second category of materials showing a PEO-like X-ray diffraction and a SEM heterogeneous aspect. However, when hydrolyzed by air humidity, macroscopic phase separation occurred as in samples from TiCl_4 . With $\text{Ti}(\text{OC}_2\text{H}_5)_4$, the phase separation was even more extensive than with TiCl_4 , since a TiO_2 gel layer formed on top of the polymer (Fig. 3c). In excess water samples, it was replaced by a fine submicron size dispersion of amorphous TiO_2 gel fibers linking planar PEO crystallite aggregates uniformly throughout the sample (Fig. 3d). Overall, in all materials hydrolyzed by slow diffusion of water, hydrolysis occurred on a smaller number of nucleation centers. Hence, phase separation occurred on a macroscopic scale. Differences between the color of the TiO_2 gel phases in samples made from TiCl_4 versus $\text{Ti}(\text{OC}_2\text{H}_5)_4$, is certainly due to the presence of Cl^- anions with the first precursor. Even the $(\text{PEO})_4\text{TiCl}_4$ sample hydrolyzed by air humidity, which belonged to a third category with an X-ray amorphous pattern, was macroscopically phase separated. The amorphous X-ray appearance of both phases is due to the high TiCl_4 proportion leading to abundant HCl formation during hydrolysis. Crystalline PEO polymer is known to have a comb structure [6], where the comb-like teeth consist of short-chain oligoethers that contain the Lewis-base [7]. If the teeth are too long, the materials looks like crystalline PEO, which occurred in our case for $n \geq 8$. If the teeth are too short, an amorphous structure forms, which obviously occurred with the highest TiCl_4 proportion.

In all cases, the feasibility of nanoscale hybrid composites is consistent with the fast nucleation of TiO_2 particles that remain separated from each other by the simultaneous formation of polymer aggregates in fast hydrolysis conditions. The fact that the TiO_2 nanoscale phase transformed to anatase instead of rutile during heat treatment cannot be attributed to the Cl^- anions, since these anions lead to rutile in the reference TiO_2 samples and they were not present when using the ethoxide. Rather, this is consistent with the action of backbone oxygen in the PEO network on the Ti cations. The nanoscale structure of the $(\text{PEO})_8\text{TiCl}_4$ sample

hydrolyzed in excess water is also consistent with the easy and reversible insertion of Li, as indicated in preliminary results. Further investigations are now underway to characterize and understand better the Li insertion process in these materials.

5. CONCLUSIONS

Hybrid PEO-TiO₂ materials with a range of structures from completely X-ray amorphous and SEM homogeneous to completely phase separated were synthesized. This could be achieved by controlling the hydrolysis process and the nature of the precursor. Nanoscale TiO₂ gel-PEO composites were obtained by hydrolysis with excess water. Slow hydrolysis by air humidity always produces macroscopic heterogeneity.

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