Low-temperature synthesis of nano-TiO$_2$ anatase on nafion membrane for using on DMFC

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Abstract. Low-temperature synthesis of 60-70°C of anatase nanocrystalline titanium dioxide TiO$_2$ using sol-gel technique on Nafion membrane is investigated and characterized. Titan tetraisopropoxide (TTIP) is used as precursor and ethanol as the solvent. The best precursor to solvent weight ratio has been used for the synthesis of nano-TiO$_2$ particles. The X-ray diffractograms and TEM images show the formation of anatase structure of nanocrystalline TiO$_2$ at low temperatures as shown with average particle size below 12 nm. The films deposited by spin coating technique using these nanoparticles show the crystalline and porous nature of the films. The nano-TiO$_2$ film as shown can be used to reduce the cross-over permeation of methanol through the PEM and increase electric power of the DMFC.

Keyword: TiO$_2$ anatase, sol-gel technique, nanoparticles.

1. Introduction

The fabrication of nanocrystalline titanium dioxide (TiO$_2$) has recently attracted much attention in terms of their versatile applications in solar cells, fuel cells, electrical and photocatalytic systems because it is highly stable, non-toxic and has a suitable redox potential for photodegrading pollutants. Several studies have focused on the use of TiO$_2$ nanoparticles for the purposes of improving the catalytic efficiency with respect to the high surface-to-volume ratio. The development of the immobilization technique that can maintain high surface area and excellent physicochemical properties of TiO$_2$ for photocatalysis is thus required.

In recent years, a great interest in nanocrystalline TiO$_2$ films has been growing, especially for use in fuel cell (FC) and also direct methanol fuel cell (DMFC) as well. Many works have been published on the preparation of titania thin films using sol-gel technique, direct deposition from aqueous solution, sputtering technology, ultrasonic spray pyrolysis and hydrothermal crystallization. The sol-gel technique of preparing TiO$_2$ thin film on the substrates has many advantages over other methods such as chemical vapour deposition (CVD), plasma spraying, anodization and thermal oxidation of Ti metal mainly because of the following reasons: (1) no special apparatus are required, (2) uniform multicomponent films can easily be formed if a homogeneous solution is available, (3) phase structure of film can be controlled, in this case TiO$_2$ (anatase) can be obtained, (4) the resultant films may be characterized by structure of a gel with a large specific area characteristic. Recently, TiO$_2$ thin films of high specific area were also reported to be obtained from a TiO$_2$ sol prepared by hydrothermal treatment of peroxotitanic acid sol or alkoxide derived TiO$_2$ gel [3].
In this work, we present results of investigations on processing and structural characteristics of TiO$_2$ thin films deposited on glass and Nafion membrane substrates at very low temperatures of 60°C by sol-gel technique using polyethylene glycol (PEG) as a template. An application of this thin film on Nafion as a special polymer substrate for using in DMFC shown above need such low temperature in processing due to properties of Nafion. The influences of concentration and type of PEG template, the amount of water added, the complexing agents and solvents were involved in this study because of the morphologies of thin films are sensitive to them. One of the main impediments to the practical realization of the DMFC as a power source is cross-over of methanol through the polymer electrolyte Nafion. The methanol permeation reduces the fraction of useful methanol since the methanol passed to the cathode is converted into carbon dioxide leads to additional losses so that the electric power decreases. In fact, TiO$_2$ nanocrystalline thin film on Nafion membrane can reduce the methanol permeation through the polymer electrolyte and then increase significantly the electric power of DMFC. We will show in this work very good results of low-temperature synthesis at ~60°C of nanocrystalline TiO$_2$ anatase with some characterizations included.

2. Experimental

Low-temperature synthesis of nanocrystalline TiO$_2$ anatase is really a very big problem when using sputtering technology, CVD method. Temperatures used in those synthesis methods usually are known at about 300°C and higher for getting crystalline anatase. In this work sol-gel technique was used with glass and Nafion substrates and we got a very good result of nanocrystalline at low-temperature of 60°C. Titanium tetraisopropoxide (TTIP) (98% Merck), ethanol (99.5%), HCl (37%), water and PEG 600 were used as the starting materials. Water and 3% of PEG 600 (average molecular weight of 600) were then introduced to the mixture. All additions were accompanied by vigorous stirring at 80°C to allow the formation of a stable, homogenous and transparent sol solution.

Following the process, titania sol formed by the procedure shown above was deposited on the substrates of glass and Nafion N117 membrane by spin coating. The substrates coated by titania sol were taken out and dried at 60°C in a vacuum dryer machine for 8 hours with flow chart of preparation as shown in detail in figure 1 below. The sol solutions and PEG prepared at 3 different pH of 1.5, 2.0 and 1.0 before spin coating were shown in figure 2, respectively.

**Figure 1.** Flow chart of preparation of nanocrystalline TiO$_2$ anatase by sol-gel technique.

**Figure 2.** Sol solution and PEG prepared at different pH before spin coating.
For application of TiO₂ coated Nafion membrane shown above to direct methanol fuel cell (DMFC), protonic conductivity measurements were performed on the membrane in a typical two electrode cell at different temperatures. A sample of the membrane (1.5 cm in diameter) was placed between two platinum electrodes and measured with AC potentiostatic condition. Methanol permeability was measured by electrochemical technique. A 1M C₂H₅OH solution was pumped into the anode side of the cell. The reaction occurring at the cathode is the oxidation of methanol that crosses through the membrane. When the applied voltage is sufficient enough to oxidize rapidly all the methanol diffusing to the cathode side, and a limiting current is achieved. The diffusion coefficient of methanol can be easily estimated from the limiting current.

3. Results and discussion
Nanocrystalline TiO₂ anatase was well prepared at low temperatures by sol-gel technique on Nafion membrane substrate. Simple hydrolysis with water was conducted at an ageing temperature of 70°C. This temperature was used as it has been reported elsewhere [4] to be sufficient for the formation of highly crystalline anatase nanoparticles. The transmission electron microscopy (TEM) images of the TiO₂ particles of our samples on Nafion membrane were shown in figure 3 with the average particle diameter is bellow 20 nm according to different pH of 1.0, 1.5 and 2.0 sol solution as described, respectively. And that the above PEG aided sol-gel process produce a very stable colloidal solution. As water is added together with PEG in the hydrolysis mixture, some water molecules as known will associate with the PEG through hydrogen bonding. The sol particles formed by the sol-gel reaction are covered by the PEG chains to form particle-PEG complex [5]. Physical cross-linking and agglomeration of these particulate complexes leads to an inorganic polymer composite.

![Figure 3. TEM images of nanoparticles of TiO₂ anatase prepared at (a) pH = 1 (b) pH = 1.5 and (c) pH = 2 of sol solutions show best result at pH = 1 with homogeneous nanoparticle size as shown.](image-url)
Thin films of TiO$_2$ were formed on the Nafion membrane by spin coating. The titania content was controlled by the TiO$_2$ concentration in sol and the coated times. The results show that the titania content increases with the TiO$_2$ concentration in the sol. When the TiO$_2$ concentration in the sol is more than 1.5 wt.%, the titania content increases rapidly. This may be caused by an increase in viscosity with titania content.

X-ray diffraction pattern of TiO$_2$ nanoparticles was performed as shown in figure 4 with peaks for the anatase phase and those for the rutile phase not observed naturally. This result indicates that the powder consists of nanocrystalline TiO$_2$ anatase with all anatase peaks as shown. In figure 4, the upper reference of XRD of anatase and rutile phase and the lower is our powder sample of TiO$_2$ with corresponding anatase peaks. By contrast, a clear peak at $2\theta = 25.8$ (101 anatase) is subjected to the ageing treatment at very low temperature of 60°C instead of 300°C and higher with other method preparation. This is clearly the characteristic peak of the anatase phase. All the clear peaks in figure 4 could be indexed as TiO$_2$ anatase as they basically all in agreement with those of the standard anatase. Those results show that thin solid film of TiO$_2$ on Nafion membrane prepared by sol-gel technique as described above is single anatase phase of nanosize TiO$_2$ particles. The nano TiO$_2$ thin films is dense and appears to be well attached to the membrane with no cracks when observed in SEM and then can reduce the methanol permeation through the polymer Nafion electrolyte and then significantly increase the electric power of DMFC as we expected. As a result, the protonic conductivity decreases with increasing titania content. The methanol permeability as a function of the TiO$_2$ content was investigated and characterized with the TiO$_2$ films on the substrates.

![Figure 4. X-ray diffraction pattern of powder of nanocrystalline TiO$_2$ anatase in comparison with sample (also with rutile peaks).](image)

The results were shown as formed on the Nafion N117 membrane and also on glass substrates. The permeability of the coated membranes decreases with increasing TiO$_2$ content in our samples with different contents and temperatures. Thus, rise in temperature leads to a strong increase in permeation by factor about 3. The methanol permeability depends on temperature and about $4 \times 10^{-6}$ cm$^2$s$^{-1}$ at 26°C. One reason for this behavior is that the nanoscale titania particles cover the cracks in Nafion membrane. A nano TiO$_2$ thin film with high content in the membrane display a so called mesoporous
network texture, which hinders the permeation of methanol. With the methanol permeation data, the poor resistance to methanol cross-over of the membrane with low titania content may be due to incomplete coverage of the cracks in the membrane.

The free, non-associated water molecules are readily available to TTIP for hydrolysis in the early stages. As hydrolysis exhausts the supply of free water, water will be drawn from the associated water. The sol particles formed by the sol-gel reaction are covered by PEG chains to form particle PEG complex. Some water molecules associate with the PEG through hydrogen bonding [6]. This feature will actually loosen the PEG chains in due course.

Nanocrystalline anatase uniform sized TiO$_2$ with average particle size varied from 8 to 13 nm has been synthesized by sol-gel technique on Nafion membrane at a very low temperature of 60°C. Particle size, shape and crystallinity of the nanoparticles are found to be dependent on the reaction temperature, time and precursor to solvent ratio. The particle size and the crystallinity increased with reaction time and temperature. For reaction temperatures as described, meta-stable anatase phase product is obtained. With the increase in the reaction temperature higher and also solvent to precursor ratio, products with random shaped TiO$_2$ nanoparticles with mixed phase (anatase and rutile) are obtained.

4. Conclusions
Thin films of anatase nanocrystalline TiO$_2$ were formed at a very low temperature of 60°C on the Nafion membrane by a simple sol-gel and spin coating procedure. Highly crystalline TiO$_2$ anatase nanoparticles are formed in an ethanol-water solution. X-ray powder diffraction analysis shows that the TiO$_2$ particles have crystallinity that is further refined by ageing treatment at 60°C. The TiO$_2$ films on membrane that are coated by a thick titania sol is very dense and no cracks are found. The protonic conductivity of the membranes decreases with increasing titania content, but their methanol permeability is also reduced. In fact, TiO$_2$ nanocrystalline thin film on Nafion membrane described above can reduce the methanol permeation through the polymer electrolyte and then increase significantly the electric power of DMFC as an application. The titania content was controlled by the TiO$_2$ concentration in sol and the coated times.

References
[1] Wainright J S, Wang J T, Weng D, Savinell R F, Liu M 1995 J.Electrochem. Soc. 142 (7) L121
[2] Su C, Hong B Y, Tseng C M 2004 Catalysis Today 96 119
[3] Bu S J, Jin Z G, Liu X X, Yang L R, Cheng Z J 2005 J. of the European Ceramic Soc. 25 673
[4] Fujima A and Honda K 1972 Nature 37 238
[5] Shimizu K, Imai H, Hirashima H and Tsukuma K 1999 Thin Solid Films 351 220
[6] Uchida H, Mizuno Y, Watanabe M 2000 Chem. Lett. 29 1268

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