

## THE SURFACE CHARGE OF UNSUPPORTED NANO-STRUCTURED TITANIA CERAMIC MEMBRANE TOP LAYERS WITH VARYING CALCINATION TEMPERATURES

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### ABSTRACT

*Titania is one of the most preferable ceramic membrane materials of superior durability (as zirconia) when compared to that of other ceramics, e.g. alumina or silica. The surface charge of the membrane top layer is an important parameter of the separation performance of the multilayer ceramic membrane due to the Donnan exclusion mechanisms. In this study, the change of the surface charge of unsupported nano-structured titania top layer is investigated with calcination temperature variation. The effect observed indicates the possibility of preparation of tailor-made top layers for multilayer ceramic membranes.*

*Keywords:* titania, membrane, surface charge, calcination.

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### INTRODUCTION

Titania (TiO<sub>2</sub>, titanium dioxide) is an important ceramic material in the production of multilayer ceramic membranes containing some other oxides like alumina (Al<sub>2</sub>O<sub>3</sub>), silica (SiO<sub>2</sub>) and zirconia (ZrO<sub>2</sub>) [1 - 4]. These membranes mostly consist of a support and a top layer (and an intermediate layer when necessary) [1 - 3]. The support is mainly responsible for the mechanical strength, while the top layer usually of a finer structure (smaller pores) provides the separation itself [3].

The sol-gel method can be used for the formation of a top layer enabling nano particulates preparation in the form of a sol [1, 5 - 7]. The latter are obtained through reactions of alkoxides hydrolysis and condensation [1, 2, 8]. They can be coated on the support (or intermediate layer). The subsequent drying (gel formation) and heat treatment (calcination) result in the formation of a homogeneous layer of a very fine microstructure as shown in Fig. 1 [1]. The SEM micrograph presented shows the nano-structured top layer (particulates less than 5nm) on top of a support which consists of bigger

particles (100 nm - 200 nm).

There are two mechanisms of separation during the pressure-driven filtration: size exclusion and Donnan exclusion. The first one refers to the screening of the particles which are bigger in size than the pores of the membrane (the top layer). The Donnan exclusion defines the rejection of particles/species/ionic groups (e.g. peptides, ions) of a surface charge different from that of the membrane surface (the top layer) [1, 2]. The Donnan exclusion mechanism which in fact refers to repulsion of similarly-charged particulates (negative-negative or positive-positive) or attraction of particulates of an opposite charge is more effective in terms of separation when the particles to be separated are small (of a low molecular weight) as in ultrafiltration (UF) and nanofiltration (NF). It is reported that the phosphate rejection of a ceramic membrane of a MWCO (molecular weight cut-off) value of 3 kDa is greater than that of a MWCO value of 1 kDa due to the higher negative surface charge of the membrane of a higher MWCO (i.e. of larger pores) [9]. The finer pores of 1 kDa MWCO membrane are not as efficient as those of 3 kDa MWCO

membrane in case of separation of negatively charged phosphate ions. This illustrates the importance of the Donnan exclusion mechanism of filtration of relatively small charged species.

This study reports the preparation of unsupported nanostructured titania membrane top layers by the sol-gel method. The sol is dried and heat treated (calcined) at different temperatures in the range of 400°C - 550°C. The surface charges of the top layers are determined in order to investigate the possibility of preparing membrane top layers of different surface charges. The latter may provide the preparation of membranes of varying separation capabilities following the Donnan exclusion mechanism.

## EXPERIMENTAL

The titania sol was prepared following the previous description [5, 6, 10]. Titanium propoxide (70 % in propanol, Sigma) was used for the sol preparation together with 2-propanol, nitric acid, acetyl acetone (acac) and deionized water of the mol ratios 1:13:0.057:2:2, respectively. The sol was prepared via dropwise addition of the acid-alcohol mixture to the alkoxide-acac-alcohol mixture. The acac was used as a stabilizer to control the rates of hydrolysis and condensation reactions taking place in the course of the polymeric sol preparation. The average particle sizes of the prepared sols were determined via laser light scattering particle size distribution analysis

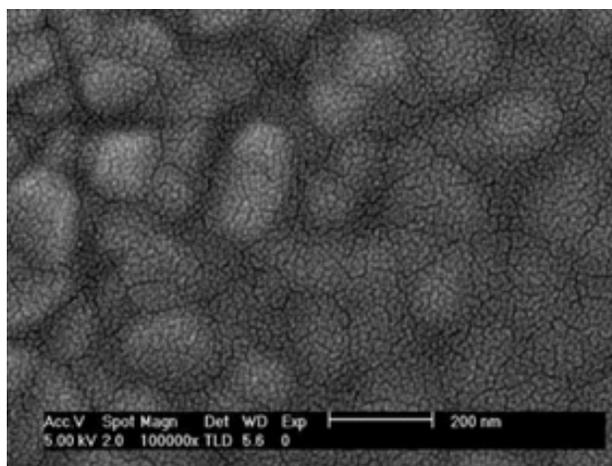


Fig. 1. The SEM (scanning electron microscope) micrograph showing the surface of a ceramic membrane [1].

(Zetasizer HSA3000, Malvern Co., UK).

The sols were dried in petri dishes to form an uncalcined membrane top layer prior to calcination. The latter was performed within 120 min (2 h) in the temperature range of 400°C - 550°C (Carbolite CWF1300). The crystallographic structures of the calcined unsupported titania layers obtained at different temperatures were determined via X-ray diffraction analysis (XRD) (CuK $\alpha$ , Philips Expert Pro). The surface charge (the zeta potential) of the calcined unsupported titania membrane top layers was determined via laser light scattering electrophoresis (Zetasizer 3000HSA, Malvern, Co., UK). The corresponding samples were prepared by dispersing titania in potassium chloride solution ( $10^{-3}$  M KCl, initial pH of 7.4) using an ultrasonic bath.

## RESULTS AND DISCUSSION

The average particle size (APS) of the titania sol is found equal to  $2.9 \pm 0.1$  nm, with a polydispersity index of 0.2. It shows a narrow particle size distribution of the particulates in the titania sol. The APS of the sol prepared is just a few nanometers because of the presence of a stabilizer (acac) controlling the hydrolysis and condensation reactions rate.

The zeta potential (surface charge) of the titania unsupported membrane top layers calcined at different temperatures are determined in a neutral KCl solution (pH of 7.4). The results are as shown in Fig. 2. There

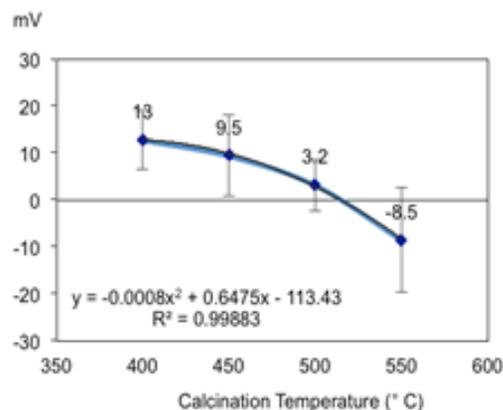


Fig. 2. The surface charge (zeta potential) of the unsupported titania membranes calcined at different temperatures (samples dispersed in  $10^{-3}$  M KCl solution with initial pH value of 7.4.)

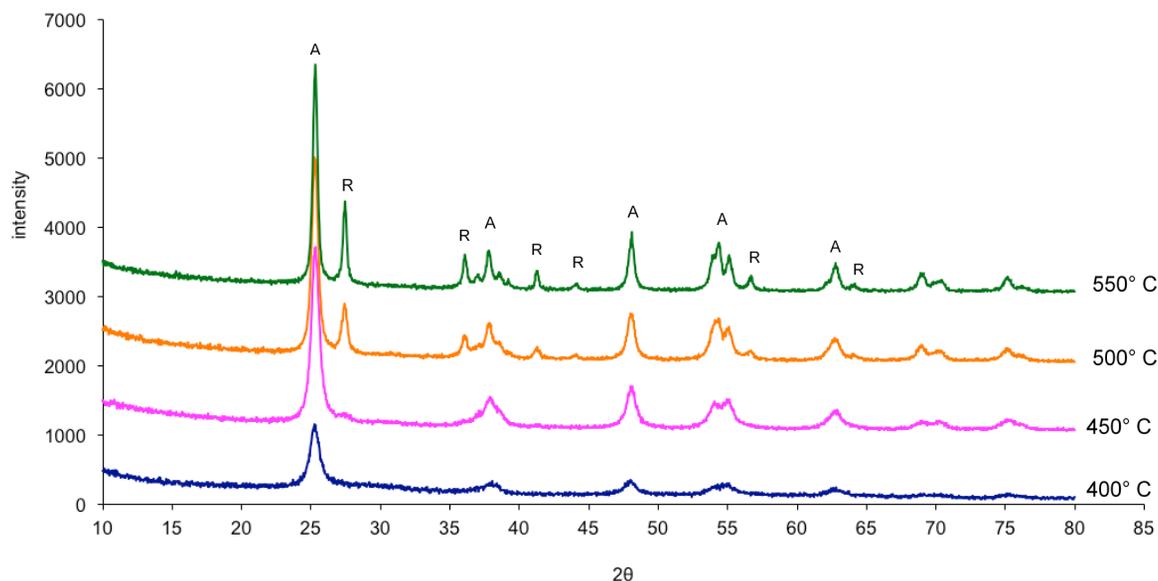


Fig. 3. XRD analysis data for unsupported titania membrane top layers calcined at different temperatures via TiAcac sol (A: anatase, R: rutile).

is a continuous decrease of the titania surface charge with the calcination temperature increase throughout the chosen temperature range.

The crystal structures of the prepared nanostructured unsupported titania top layers are analysed via XRD. The patterns obtained are shown in Fig. 3. They indicate the formation of an anatase phase at lower calcination temperatures and initiation of rutile phase formation with further temperature increase.

The crystallite sizes of the titania calcined at varying temperatures are calculated via the software of the XRD instrument. They are shown in Fig. 4. It is seen that the

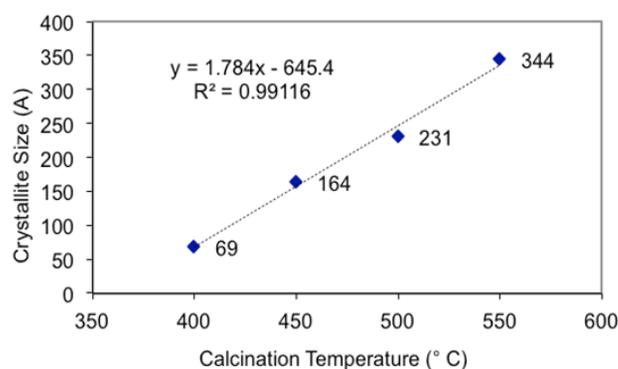


Fig. 4. The crystallite sizes (in Angstroms) at different calcination temperatures (for 120 minutes).

size increases from ~7 nm to ~34 nm with calcination temperature increase.

The change of the crystal structure of the nanostructured unsupported titania membrane top layer accompanied by a phase transformation from anatase to rutile results in a change of titania surface charge. The latter is even visible at a pH value close to neutrality (pH 7.4). It will be more considerable at more acidic and/or basic pH values. That modification of the surface charge with a controllable process parameter (i.e. calcination temperature) may be beneficial for preparation of membrane top layers of different surface characteristics.

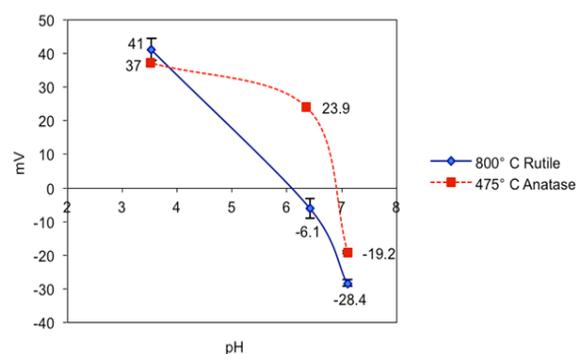


Fig. 5. The zeta potential values for pure anatase and pure rutile titania prepared via calcination of the sol at 475°C and 800°C, respectively.

The separation of ionic species of a relatively lower mass during filtration (like ultrafiltration (UF) and nanofiltration (NF)) is mostly controlled by the Donnan exclusion mechanism, rather than the size exclusion one. Therefore, multilayer ceramic membranes of titania top layers can be prepared of different surface (attraction/repulsion) properties, which determine the membrane separation efficiency and fouling behaviour.

The further zeta potential determination experiments with pure anatase and pure rutile phases of titania (which are prepared via calcination of a titania sol at 475°C and 800°C, respectively) are performed at different pH values. The results are shown in Fig. 5. The pure rutile phase has a lower isoelectric point (IEP) than that of the pure anatase phase. This shows that the surface charge (the zeta potential) of the nanostructured unsupported membrane top layer titania is dependent on the present crystal structure/phase.

## CONCLUSIONS

Titania is one of the main oxides used in preparation of top layers of multilayer ceramic membranes. Titania top layers can be prepared with varying surface charges by changing the calcination temperature. The latter has to be kept in a certain range to provide a crystalline stable top layer but not a coarse structure of relatively larger pores hampering the separation via size exclusion. The phase transformation from anatase to rutile changes the surface characteristics of the membrane top layer, which may be beneficial for preparation of membranes of different Donnan exclusion characteristics (i.e. of better separation capabilities and/or less fouling tendency).

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