First stages of nanoporous oxide growth on Ti in organic fluoride-containing electrolytes

Mina Stancheva, Martin Bojinov
Department of Physical Chemistry, University of Chemical Technology and Metallurgy,
Kl. Ohridski Blvd. 8, 1756 Sofia, Bulgaria

INTRODUCTION
• Electrochemical formation of self- ordered arrays of TiO_2 nanotubes → great interest due to their applications in sensors, dye sensitized solar cells, batteries, and even bio- implants.
• Benefits of electrochemically grown TiO_2 → fabrication of nanotube arrays of different shape, pore size, length, and wall thickness → controlling electrochemical parameters (potential, electrolyte composition and fluoride content, process duration, stirring...)

AIMS
• Investigation of anodic film growth on Ti in organic electrolyte with different amounts of fluoride by electrochemical methods
• Estimation of the chemical composition of the oxide surface
• Comparison of the model and experimental results

EXPERIMENTAL
• Electrochemical anodization in a potentiostatic regime – three-electrode configuration: pure Ti (99.9%. Goodfellow) as working electrode, Pt mesh counter electrode, Ag / AgCl / 3 M KCl reference electrode
• Electrolytes – 0.6 M and 1.1 M H_2O in ethylene glycol with the addition of 0.01, 0.06, 0.1 and 0.2 M NH_4F
• Electrochemical measurements – Autolab PGSTAT30+FRA, GPES and FRA2 software (EcoChemie)
• Steady-state current vs. potential curves (potentiostatic mode)
• Electrochemical impedance spectra → range of potentials -0.1/5.0 V, frequency range 20 mHz – 20 kHz, ac amplitude 15 mV rms
• Chemical composition of the oxide film – X-ray photoelectron spectroscopy (XPS)

RESULTS
Current vs. potential curves (Fig. 1)
• Quasi-exponential increase of the current density with potential, constant currents reached for higher potentials
• Higher fluoride content → higher current densities and higher barrier film thicknesses at constant potential (as estimated from high-frequency capacitance)
• Oxide layer thickness → increases quasi-linearly with potential

Impedance spectra (Figs 2 and 3)
• two time constants – high-frequency capacitive and low-frequency pseudo-inductive - migration of current carriers and recombination, capacitive behavior at low frequencies – modulation of film thickness (faradaic pseudocapacitance)
• the capacitance of the barrier layer decreases significantly with fluoride content, the product of ion migration resistance and current density increases slightly

X-ray photoelectron spectroscopy (Fig. 4)
Non- stoichiometric oxide, mainly Ti^{4+} and a smaller amount of Ti^{3+}, with a certain degree of hydroxylation, thickness estimates agree with those from capacitance

DISCUSSION - Kinetic model of the process (Fig. 5)
▪ Growth of the barrier film → at the metal / film interface with oxidation of the metal and generation of oxygen vacancies
▪ Consumption of these vacancies at the film / solution interface
▪ Film dissolution → chemical reaction, influenced by fluoride content
▪ Ejection of cations / generation of vacancies at the film/solution interface
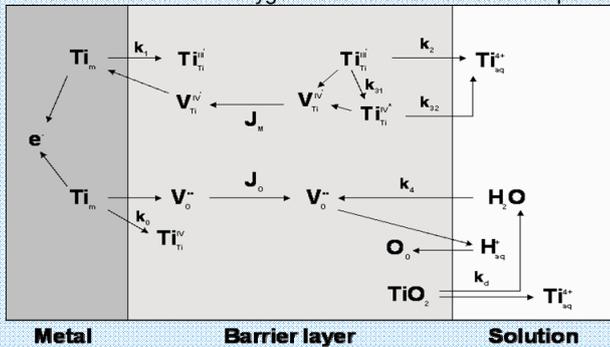▪ Recombination of cation and oxygen vacancies to recreate the perfect lattice

Fig. 5 A scheme of the processes of barrier layer formation and dissolution

Equation of current-potential curve and transfer function derived, first calculations with the model succesful in reproducing experimental behaviour (Fig.1a and 2a)

FUTURE STEPS
• *Determination of model parameters as depending on water / fluoride content*
• *Extension of the model to thicker films, nanopore initiation and growth*
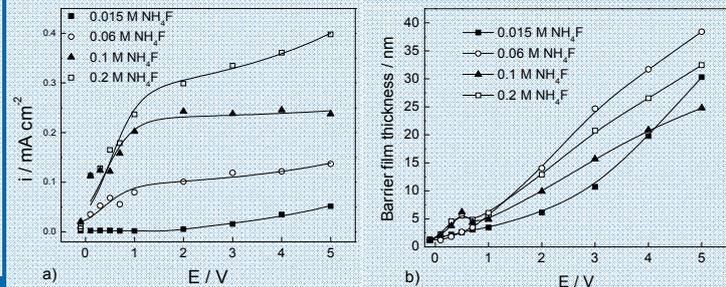

Fig. 1 a) Current vs. potential during anodization of Ti. Symbols – Experimental data, lines - calculated values according to the proposed model. b) barrier film thickness vs. potential in electrolytes with different fluoride content
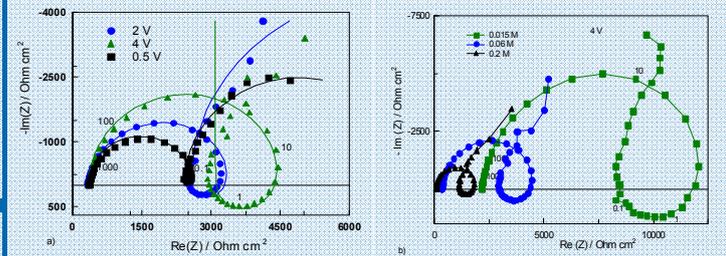

Fig. 2 Impedance spectra of Ti at a) different potentials in an electrolyte with 0.06 M NH_4F, symbols – experimental data, lines – calculated values according to the proposed model, and b) at E = 4 V in electrolytes with different fluoride content
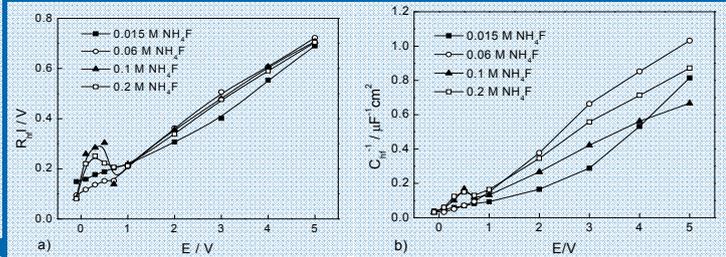

Fig. 3 R_{hf} a) and C_{hf} b) dependence of the potential obtained for different fluoride content
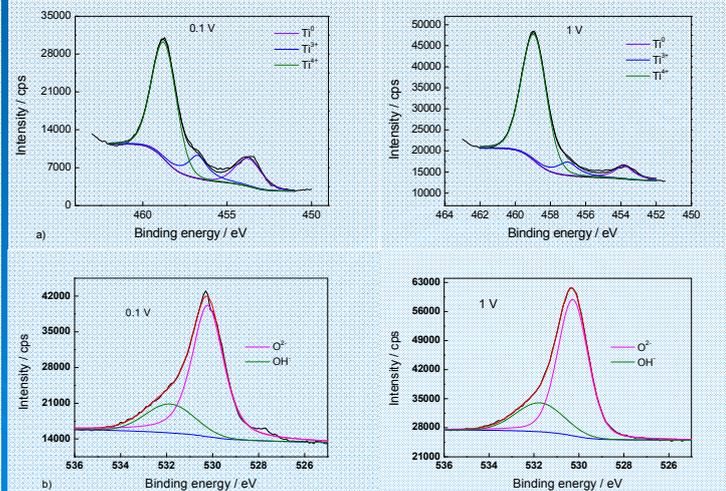

Fig. 4 Ti 2p XPS spectra a) and O1s spectra b) for TiO_2 films grown in an electrolyte with 0.06 M NH_4F and 1.1 M H_2O at different potentials