

GROWTH AND DISSOLUTION OF PASSIVE FILMS – ESTIMATION OF KINETIC PARAMETERS FROM EIS AND XPS DATA

Martin Bojinov

University of Chemical Technology and Metallurgy, Sofia, Bulgaria

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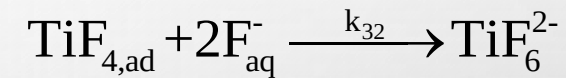
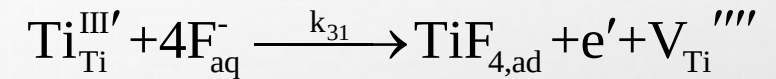
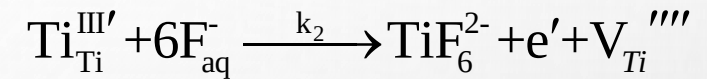
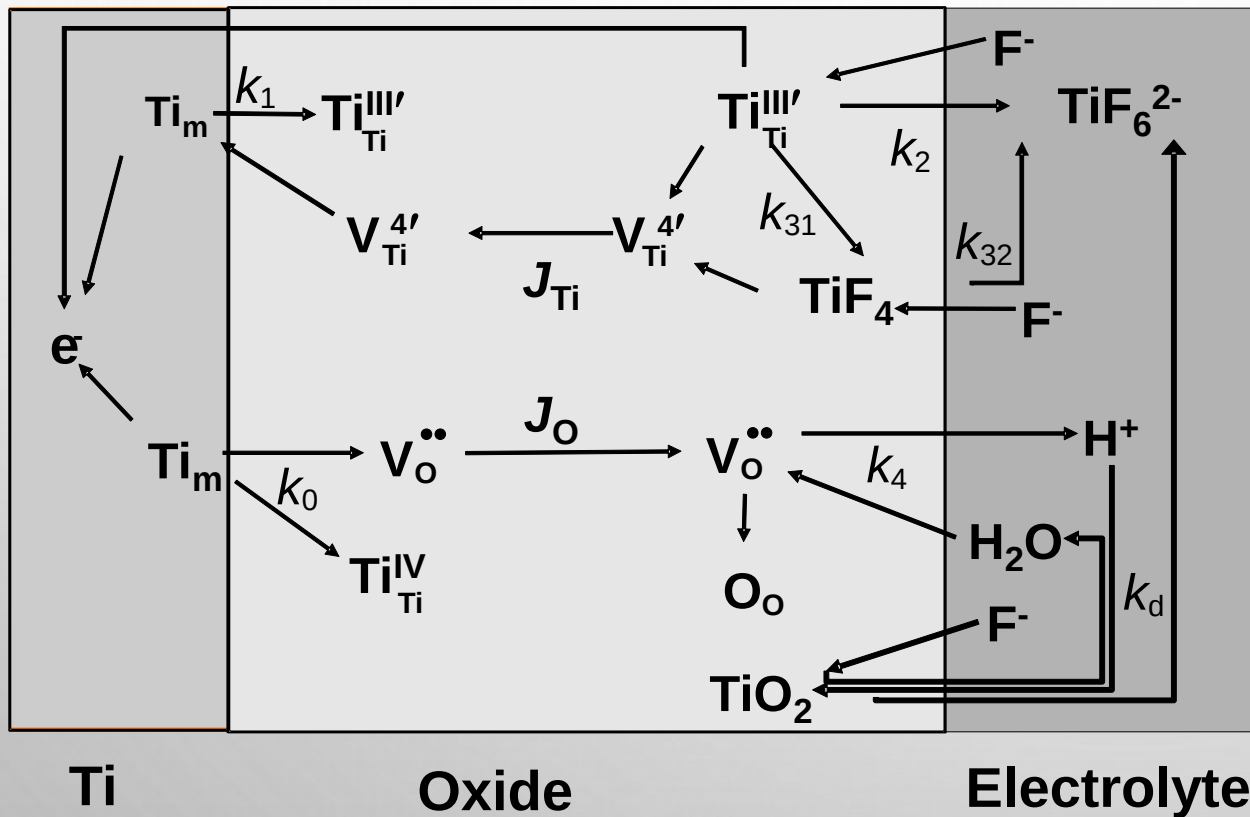
INTRODUCTION

- ELECTROCHEMICAL KINETIC MODELS FOR COMPLEX SYSTEMS → RELATIVELY LARGE NUMBER OF ADJUSTABLE PARAMETERS → NO UNAMBIGUOUS INTERPRETATION OF ELECTROCHEMICAL IMPEDANCE SPECTRA IN TERMS OF A UNIQUE APPROACH
- SIGNIFICANT PROGRESS IN OVERCOMING THIS INHERENT DIFFICULTY → CONCEPT OF MULTIPLE TRANSFER FUNCTION ANALYSIS
- AN ALTERNATIVE → IMPEDANCE MEASUREMENTS IN DIFFERENT CONFIGURATIONS
- FURTHER POSSIBILITIES → COMPARING KINETIC MODEL PREDICTIONS TO COMBINATION OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPIC AND SURFACE ANALYTICAL DATA

AIM OF THE WORK

- VALIDATION OF KINETIC MODELS BY THEIR QUANTITATIVE COMPARISON TO A COMBINATION OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPIC AND X-RAY PHOTOELECTRON SPECTROSCOPIC DATA → FURTHER CREDIBILITY OF THE ESTIMATES OF KINETIC AND TRANSPORT PARAMETERS
- TWO SYSTEMS INVOLVING PASSIVE FILM GROWTH AND DISSOLUTION – TITANIUM IN ETHYLENE GLYCOL-WATER-FLUORIDE SOLUTIONS AND ALLOY 690 IN SIMULATED PRESSURIZED WATER REACTOR COOLANT – USED AS REPRESENTATIVE EXAMPLES

TITANIUM IN EG-WATER-FLUORIDE SOLUTIONS – KINETIC MODEL



$$k_2 = k_2^0 \exp(b_2 E), k_{31} = k_{31}^0 \exp(b_{31} E)$$

MAIN EQUATIONS

$$\bar{I} = \bar{I}_M + \bar{I}_0 = 4F \frac{k_{32}^2 (\bar{k}_2 + \bar{k}_{31})^2 + k_d^2 (\bar{k}_{31} + \bar{k}_{32})^2}{(\bar{k}_{31} + \bar{k}_{32}) [k_{32} (\bar{k}_2 + \bar{k}_{31}) + k_d (\bar{k}_{31} + \bar{k}_{32})]}$$

Steady- state solution –
current vs. potential curve

Small amplitude ac solution –
impedance spectra as depending on potential

$$Z_O = Z_{O,f} + \frac{1}{j\omega C_0},$$

$$Z_{O,f}^{-1} = \frac{\Delta I_0}{\Delta E} = \frac{2\bar{I}_0 B}{\bar{L}} \left[(1-\alpha) + \frac{\bar{I}_0 S \alpha}{j\omega + \bar{I}_0 S} \right], C_0 = (\bar{I}_O + \bar{I}_M) \frac{(1-\alpha)}{\bar{I}_O \bar{E}} \frac{V_m}{4F}$$

$$Z_M = Z_{M,f} + Z_{M,F/S}, Z_{M,f}^{-1} = \frac{\Delta I_M}{\Delta E} = \frac{4\bar{I}_M B}{\bar{L}} \left[(1-\alpha) + \frac{I_0 S \alpha}{j\omega + I_0 S} \right]$$

$$Z_{M,F/S} = (4F b_2 \bar{k}_2 \bar{\gamma}_3)^{-1} \left[1 + \frac{b_{31} \bar{k}_{31} (\bar{k}_2 - \bar{k}_{31})}{\left(1 + j \left(\frac{\omega \beta_M \bar{k}_2 b_2}{b_2 k_{32} \bar{k}_2 + b_{31} \bar{k}_{31}^2} \right) \right) (b_2 \bar{k}_2 k_{32} + b_{31} \bar{k}_{31}^2 + \bar{k}_{31} \bar{k}_2 (b_2 - b_{31}))} \right]$$

$$\bar{\gamma}_3 = \frac{k_{32}^2 (\bar{k}_2 + \bar{k}_{31})}{(\bar{k}_{31} + \bar{k}_{32}) [k_{32} (\bar{k}_2 + \bar{k}_{31}) + k_d (\bar{k}_{31} + \bar{k}_{32})]}$$

$$Z = R_{el} + \left[j\omega C + \frac{1}{Z_O} + \frac{1}{Z_M} \right]^{-1}$$

PARAMETER ESTIMATION

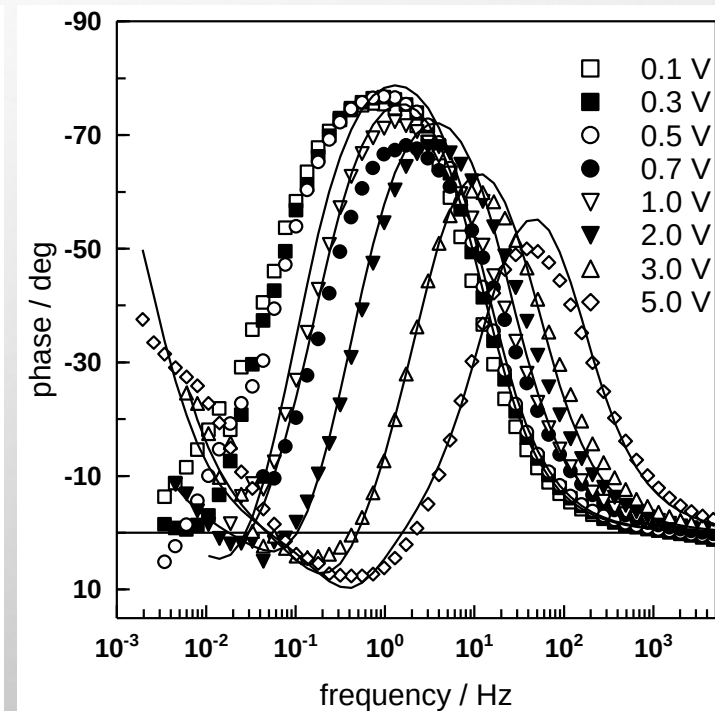
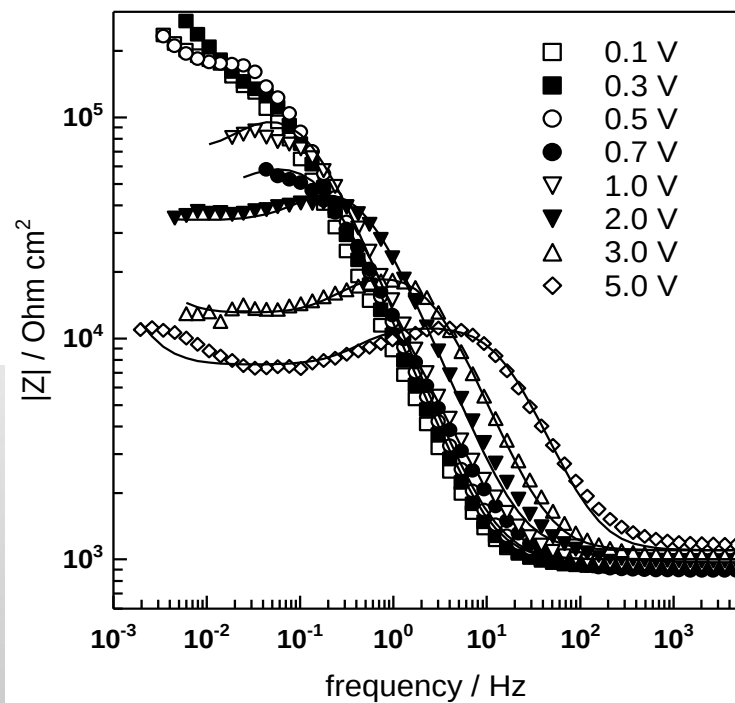
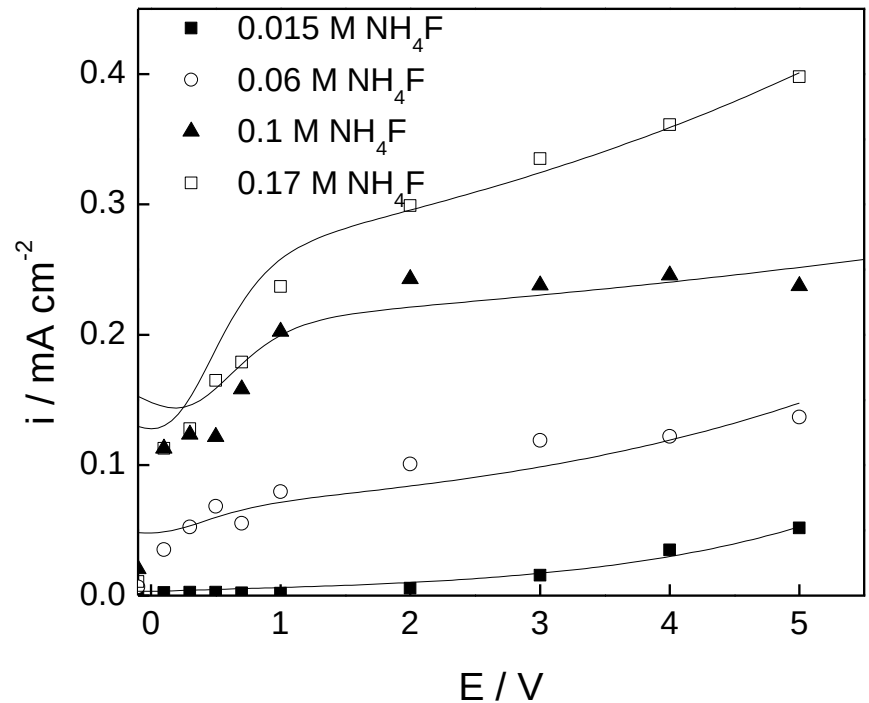
- Non-linear regression of current-potential curves → estimates of rate constants and exponential coefficients

$$(k_2^0, b_2, k_{31}^0, b_{31}, k_{32} \text{ and } k_d)$$

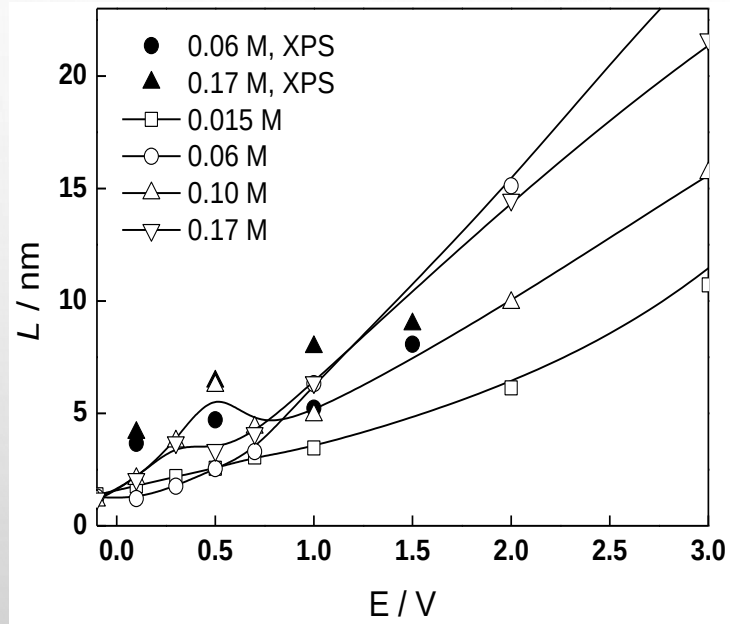
- Non-linear regression of impedance spectra in a wide interval of potential → keeping the above values constant → determination of transport/structural parameters

$$\rightarrow (E, \alpha, a, \beta, \beta_o)$$

REGRESSION RESULTS – ELECTROCHEMICAL DATA



FILM THICKNESS



EIS – from high-frequency capacitance

$$C = L_{E=0} + \frac{\varepsilon \varepsilon_0}{E} E$$

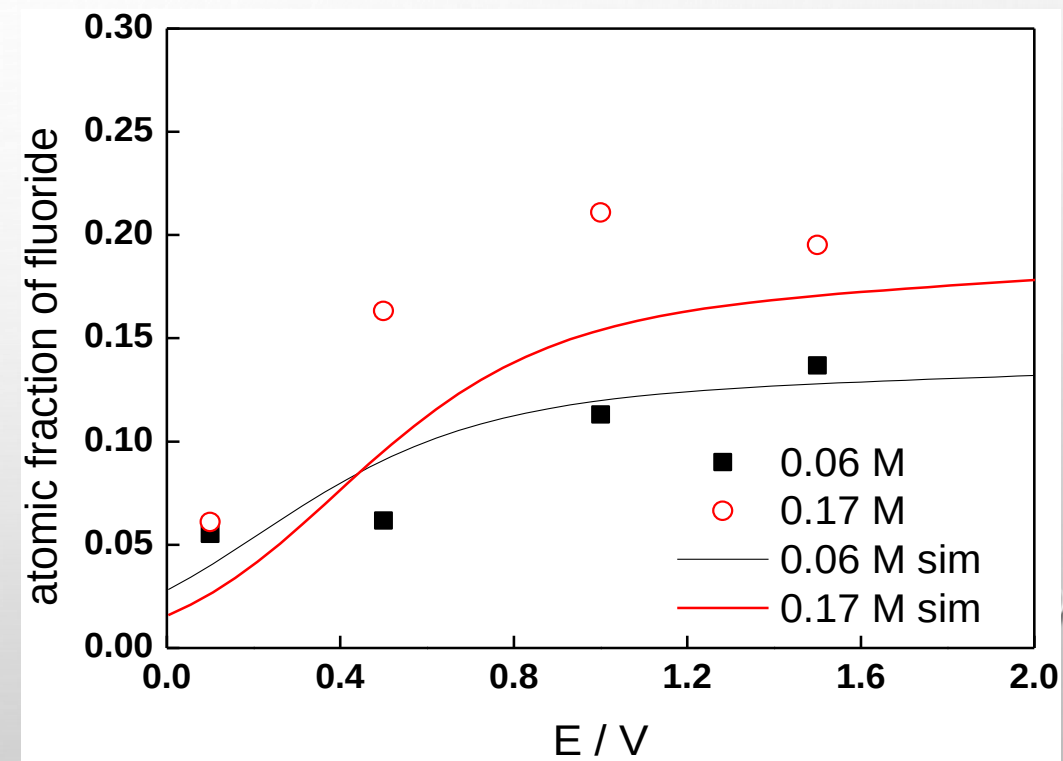
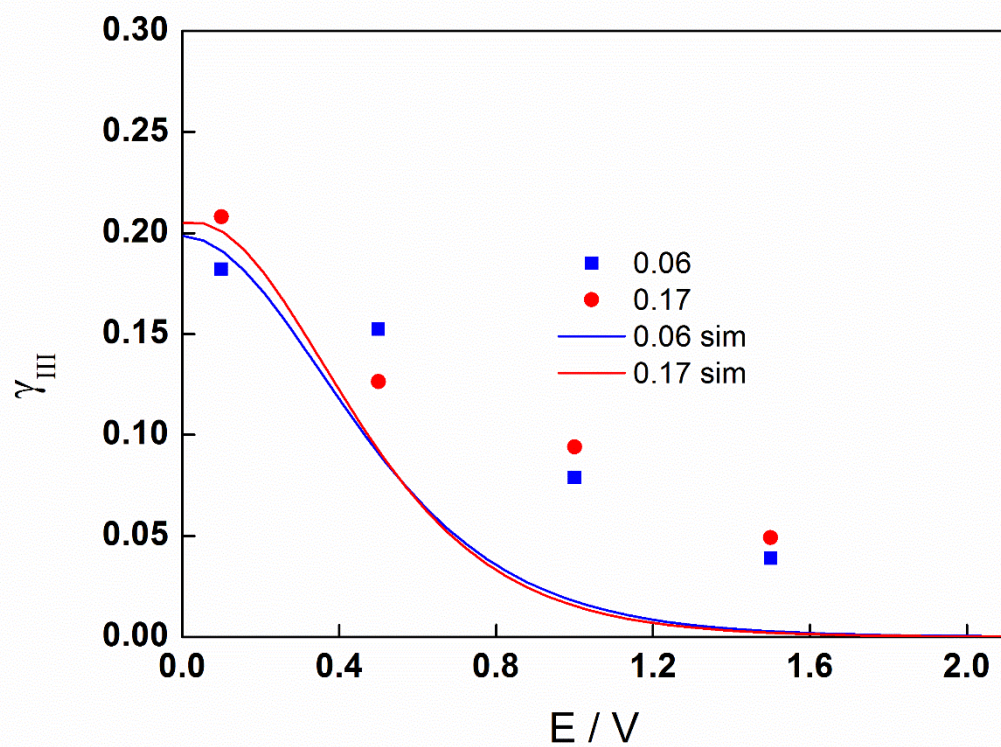
XPS – thin uniform oxide layer on an infinite Ti substrate

$$d_{ox} = \lambda_{TiO_2} \sin \beta \ln \left(1 + \frac{\rho_{Ti}}{\rho_{TiO_2}} \frac{\lambda_{Ti}}{\lambda_{TiO_2}} \frac{I_{Ti(IV)}}{I_{Ti(0)}} \right)$$

FILM COMPOSITION

$$\bar{\gamma}_{\text{Ti(III)}} = \frac{k_{32}^2 (\bar{k}_2 + \bar{k}_{31})}{(\bar{k}_{31} + \bar{k}_{32}) [k_{32} (\bar{k}_2 + \bar{k}_{31}) + k_d (\bar{k}_{31} + \bar{k}_{32})]}$$

$$\bar{\gamma}_{\text{TiF}_4} = \frac{\bar{k}_{31} k_{32} (\bar{k}_2 + \bar{k}_{31})}{(\bar{k}_{31} + k_{32}) [k_{32} (\bar{k}_2 + \bar{k}_{31}) + k_d (\bar{k}_{31} + \bar{k}_{32})]}$$



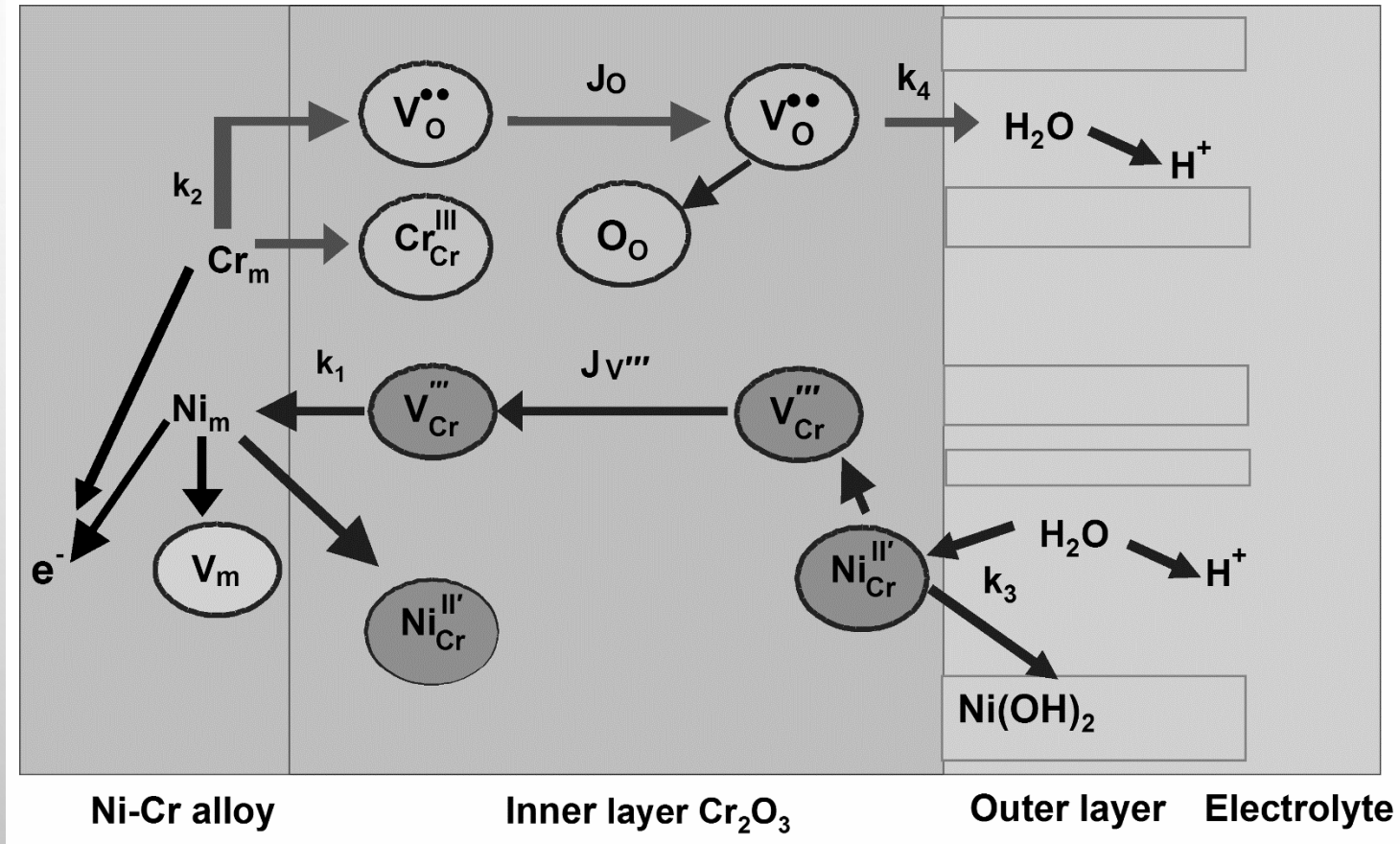
CONCLUSIONS – TITANIUM SYSTEM

- The experimental data in a broad range of potentials, fluoride concentrations and water contents described with a rather homogeneous set of kinetic parameters
- The part of the potential consumed at the film/solution interface, the exponential coefficients b_2 and b_{31} independent on fluoride and water concentration within the calculation error, preserving values typical for film covered electrodes
- The values of the field strength are within the limits of the high-field approximation used in the present treatment, being somewhat lower than those usually reported for film growth on Ti in aqueous electrolytes
- The estimates of the maximal surface concentrations of cation sites and anion vacancies are well comparable to the expected number of active sites at the film/solution interface
- The proposed model is able to reproduce the film thickness, the evolution of Ti(III) and fluoride concentrations at the oxide surface for all studied materials. Estimates of film thickness from EIS and XPS are in very good agreement, lending credibility to the procedure for the estimation of the kinetic parameters.

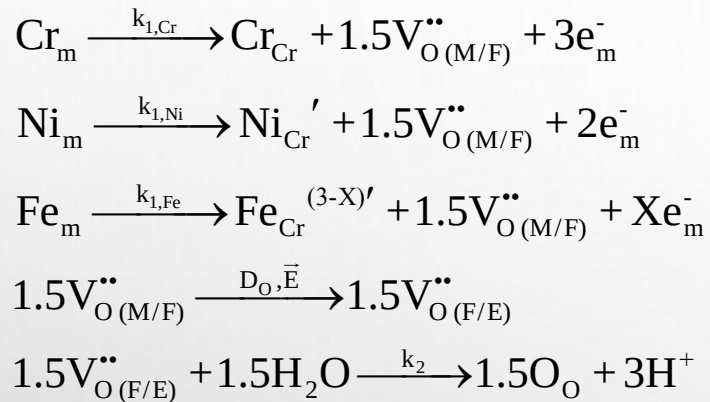
FUTURE TRENDS – TITANIUM OXIDATION

- EXTENSION OF THE PROCEDURE PROPOSED FOR PURE TI TO TITANIUM ALLOYS
- DEVELOPMENT AND TESTING OF A SIMULATION OF NANOPORE INITIATION ON THE BASIS OF THE MODEL FOR BARRIER LAYER GROWTH AND DISSOLUTION
- ESTIMATION OF REACTION AND TRANSPORT RATES DURING GROWTH OF TITANIUM OXIDE BY ATOMISTIC CALCULATIONS USING DENSITY FUNCTIONAL THEORY – ASSESSMENT OF THE RATE CONSTANTS AT THE METAL/FILM INTERFACE

ALLOY 690 IN PRESSURIZED WATER REACTOR PRIMARY COOLANT – KINETIC MODEL



MAIN EQUATIONS – ELECTROCHEMICAL BEHAVIOR



$$Z = R_{el} + Z_f + Z_{F/E} = R_{el} + (Z_e^{-1} + Z_i^{-1})^{-1} + \frac{1}{R_{F/E}^{-1} + j\omega C_{F/E}}$$

$$Z_f = (Z_e^{-1} + Z_i^{-1})^{-1}$$

$$Z_e \approx \frac{RT}{2j\omega F \vec{E} L C} \ln \left[\frac{1 + j\omega \frac{RT}{F^2 D_e} \frac{k_2}{k_1} \epsilon \epsilon_0 \exp\left(2 \frac{F \vec{E}}{RT} L\right)}{1 + j\omega \frac{RT}{F^2 D_e} \frac{k_2}{k_1} \epsilon \epsilon_0} \right]$$

$$Z_i = R_t + \frac{RT}{8F^2 \frac{F \vec{E}}{RT} D_o k_1 (1-\alpha) \left[\frac{1}{k_2 \exp(2KL)} + \frac{RT}{2F \vec{E} D_o} \right] \left[1 + \sqrt{1 + \frac{j\omega (RT)^2}{(F \vec{E})^2 D_o}} \right]}$$

MAIN EQUATIONS – FILM COMPOSITION AND THICKNESS

Transport equations

$$\frac{\partial y_{Cr}}{\partial t} = D_O \frac{\partial^2 y_{Cr}}{\partial x^2} + \frac{3F\vec{E}D_O}{RT} \frac{\partial y_{Cr}}{\partial x}$$

$$\frac{\partial y_{Fe}}{\partial t} = D_O \frac{\partial^2 y_{Fe}}{\partial x^2} + \frac{XF\vec{E}D_O}{RT} \frac{\partial y_{Fe}}{\partial x}$$

$$\frac{\partial y_{Ni}}{\partial t} = D_O \frac{\partial^2 y_{Ni}}{\partial x^2} + \frac{2F\vec{E}D_O}{RT} \frac{\partial y_{Ni}}{\partial x}$$

Boundary conditions

$$y_{Cr}(x, 0) = y_{Cr,a}, y_{Ni}(x, 0) = y_{Ni,a}, y_{Fe}(x, 0) = y_{Fe,a}$$

$$y_{Cr}(0, t) = y_{Cr,a}, y_{Ni}(0, t) = y_{Ni,a}, y_{Fe}(0, t) = y_{Fe,a}$$

$$y_{Cr}(L, t) = \frac{k_{1,Cr}}{V_{m,MO}} \left[\frac{1}{k_2} + \frac{RT}{3F\vec{E}D_O} \right]$$

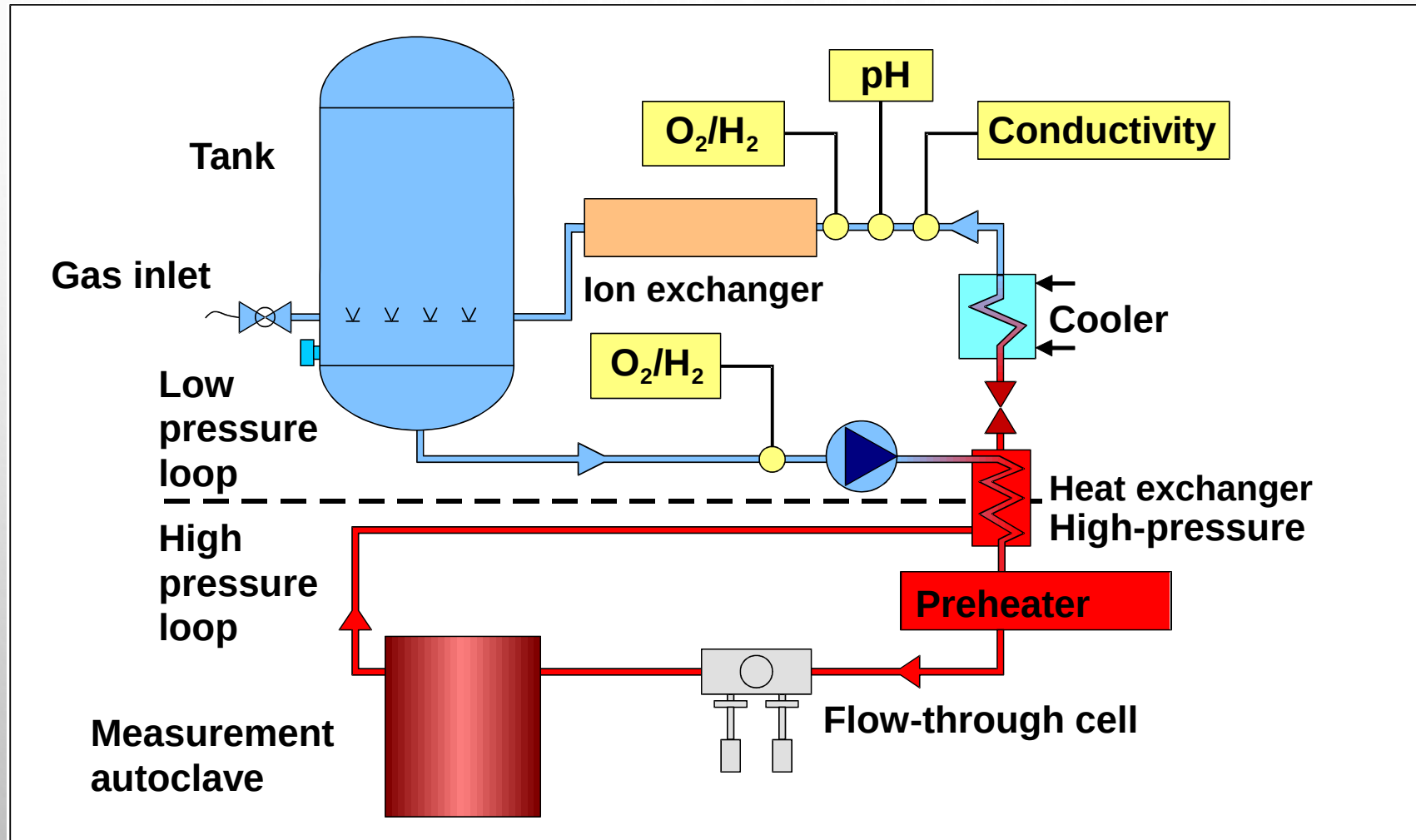
$$y_{Fe}(L, t) = \frac{k_{1,Fe}}{V_{m,MO}} \left[\frac{1}{k_2} + \frac{RT}{XF\vec{E}D_O} \right]$$

$$y_{Ni}(L, t) = \frac{k_{1,Ni}}{V_{m,MO}} \left[\frac{1}{k_2} + \frac{RT}{2F\vec{E}D_O} \right]$$

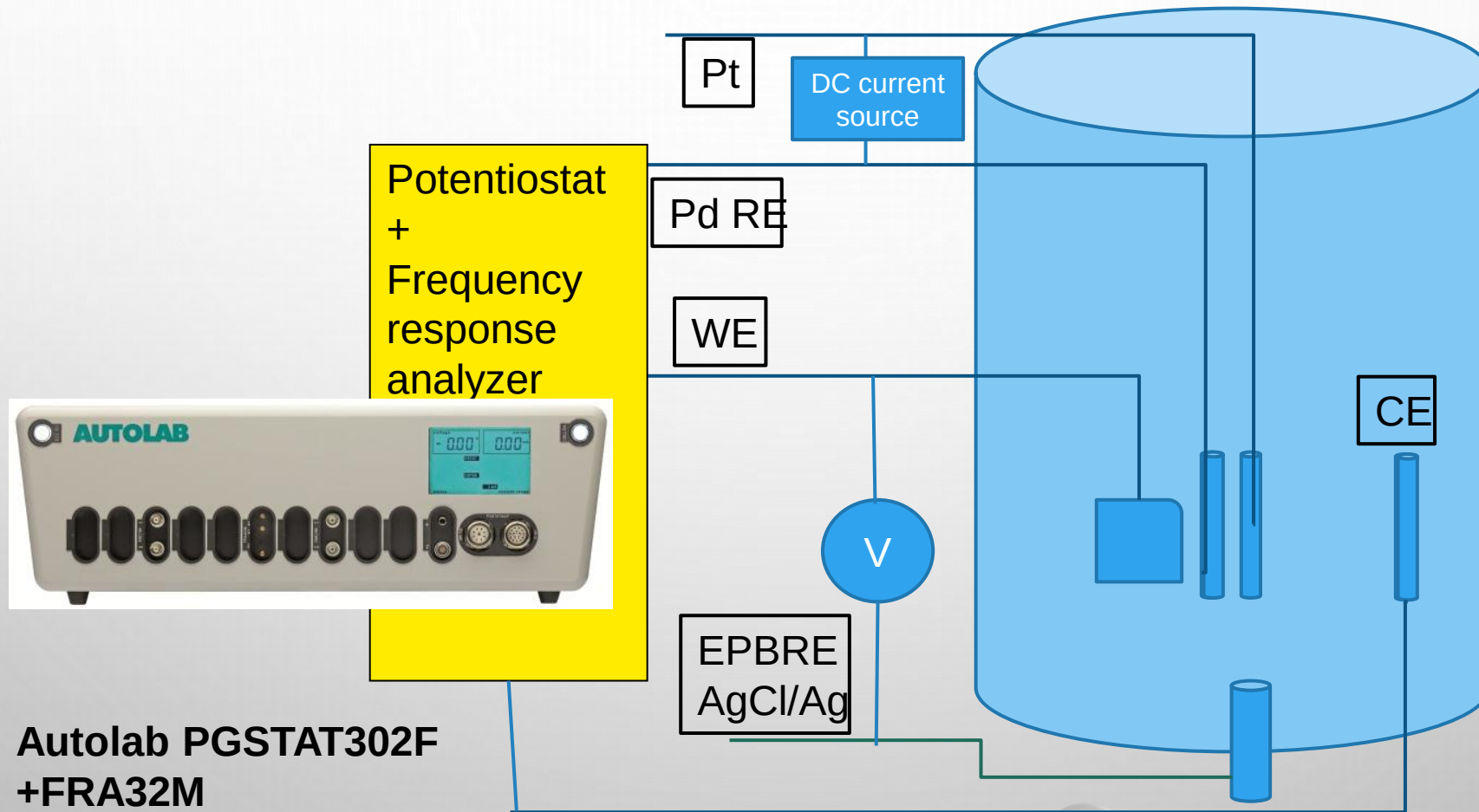
Film growth with time

$$L(t) = L(t=0) + \frac{1}{b} \ln \left[1 + V_{m,MO} k_1 b e^{-bL(t=0)t} \right], b = \frac{3\alpha_1 F \vec{E}}{RT}$$

TYPICAL MEASUREMENT LOOP



MEASUREMENT AUTOCLAVE – DETAILS



PROCEDURE FOR PARAMETER ESTIMATION

1. Impedance spectra for Alloy 690 fitted to model equations → values of the parameters

$$C, k_1, k_2, D_O, \vec{E}, R_{F/E} \text{ and } C_{F/E}$$

estimated as depending on exposure time and HFT chemistry

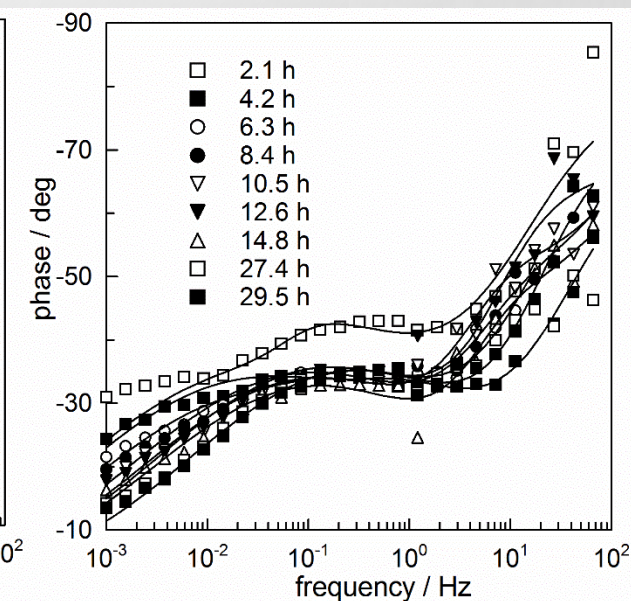
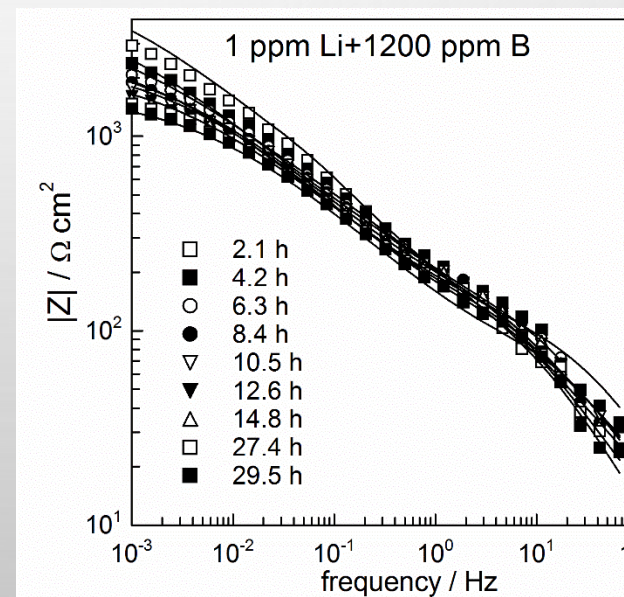
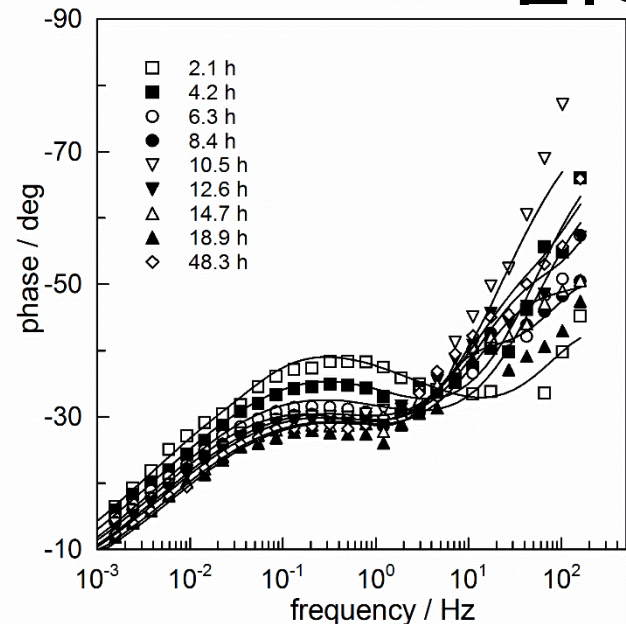
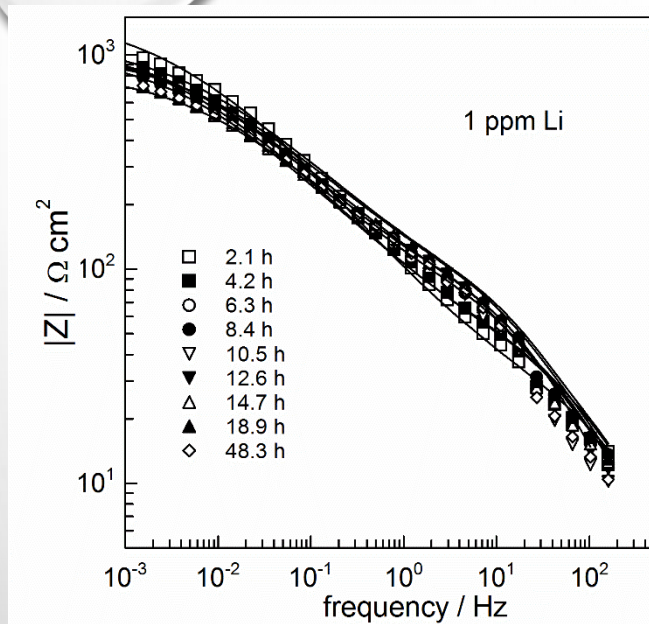
2. Estimates for the rate constants of oxidation of individual constituents at the alloy/film interface → quantitative comparison of the XPS depth profile data with the model equations.

The estimates of the rate constant k_1 obtained from the fitting of the electrochemical data were used to introduce the following restriction:

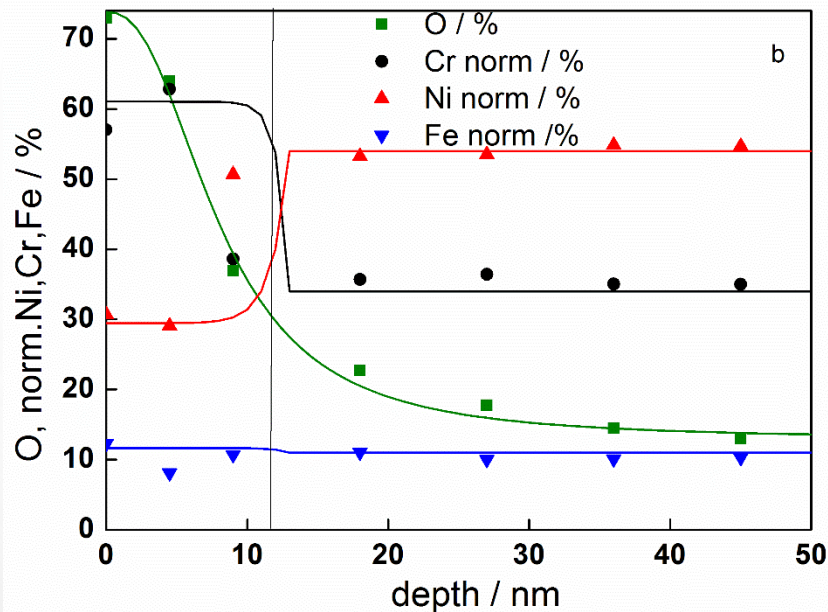
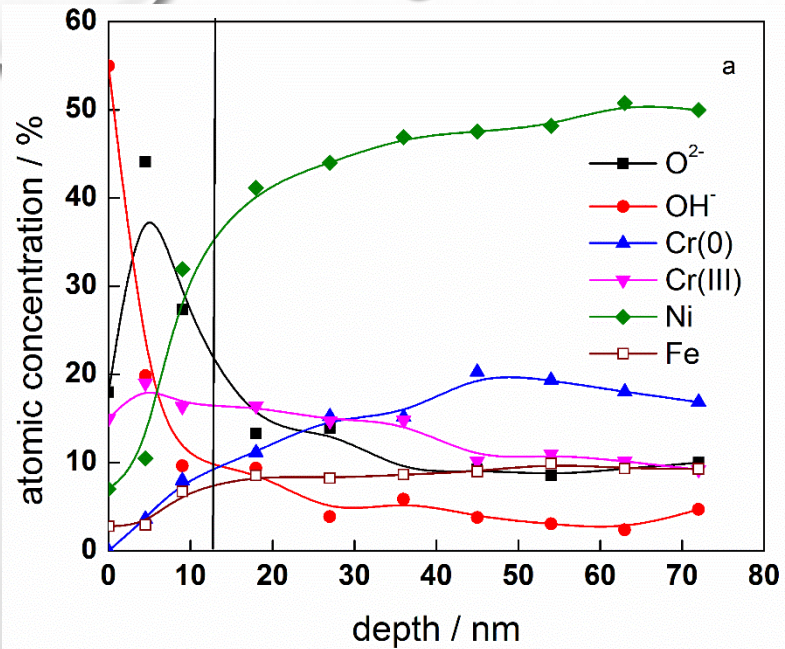
$$k_1 = k_{1,Cr} y_{Cr,a} + k_{1,Ni} y_{Ni,a} + k_{1,Fe} y_{Fe,a}$$

COMPARISON WITH EXPERIMENTAL DATA -

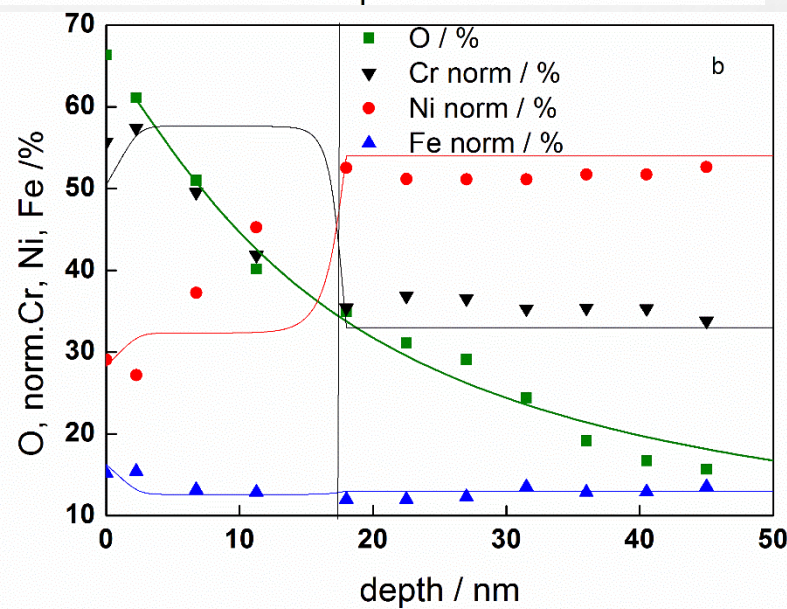
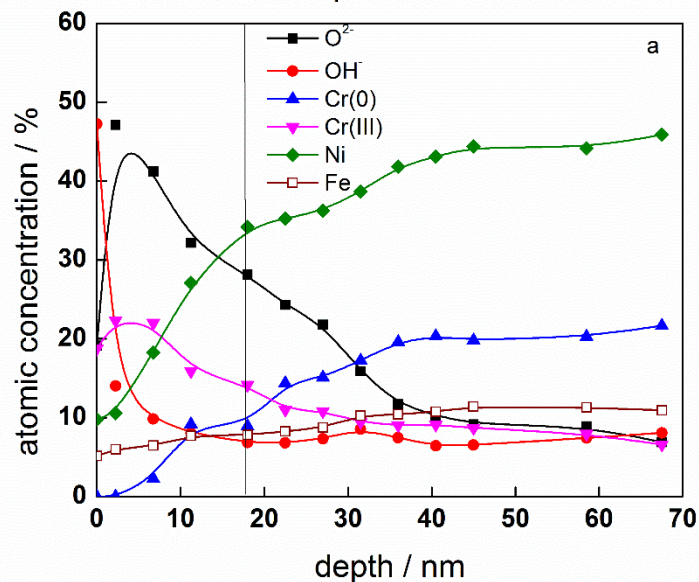
EIS



COMPARISON TO EXPERIMENTAL DATA - XPS



1 ppm Li



1 ppm Li + 1200 ppm B

CONCLUSIONS – ALLOY 690 IN PWR PRIMARY COOLANT

- A quantitative procedure to interpret simultaneously electrochemical impedance and surface analytical results → successfully used to obtain of the interfacial rate constants of oxidation of individual alloy constituents (Ni, Cr and Fe), the diffusion coefficient of oxygen vacancies, as well as field strength in the growing oxide
- Main conclusion → increasing LiOH concentration in the simulated PWR water → higher dissolution rates, faster metal oxidation and transport rates through the oxide → the formed oxide is found to be the more defective, the higher the concentration of Li in the electrolyte is
- On the other hand, boron added as H_3BO_3 was found to have a beneficial effect that counteracts the accelerating influence of LiOH.

FUTURE TRENDS – CONSTRUCTION MATERIALS IN LIGHT WATER REACTORS

- DEVELOPMENT OF A 2-D APPROACH TO TREAT OXIDATION ON INDIVIDUAL GRAINS AND GRAIN BOUNDARIES
- EXTENSION OF THE MODEL TO PREDICT CORROSION RELEASE IN LIGHT WATER REACTOR PRIMARY COOLANT
- COMPARISON OF THE MODEL WITH ATOMISTIC CALCULATIONS OF THE REACTION AND TRANSPORT RATES IN CHROMIUM OXIDE AND SPINEL OXIDES SUCH AS MAGNETITE AND CHROMITE

ACKNOWLEDGMENTS

- DDVU-02-103 “NANOPOROUS ANODIC OXIDES AS NEW GENERATION OF OPTICALLY ACTIVE AND CATALYTIC MATERIALS” (NOXOAC, 2010-2014)
- FP7-232612 “PREDICTION OF THE EFFECTS OF RADIATION FOR REACTOR PRESSURE VESSEL AND IN-CORE COMPONENTS USING MULTI-SCALE MODELLING-60 YEARS FORESEEN PLANT LIFETIME (PERFORM 60, 2009-2013)”
- SAFIR2010 AND SAFIR 2014 - FINNISH RESEARCH PROGRAMMES ON NUCLEAR POWER PLANT SAFETY