Characterization and properties of electrodeposited molybdenum oxides

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Introduction

- Molybdenum oxides have shown significant potential for application → catalysis, solar selective absorption, gas sensing and electroanalysis
- Electrochemical deposition → a method for fabrication of molybdenum oxides that offers significant advantages: ability to grow uniform coatings on structures of arbitrary shape, kinetic control by the amount of charge passed, and thermodynamic control by variation of the electrode potential
- Investigations on the electrodeposited molybdenum oxide thin films on different substrates → solution pH has an important role in determining their composition and structure → more homogeneous films are formed in nearly neutral and mildly alkaline solutions?

Aims

- Investigation of the processes of electrodeposition of molybdenum oxides from weak alkaline solutions (pH 8–10)
- Characterization of their chemical composition and electrochemical properties

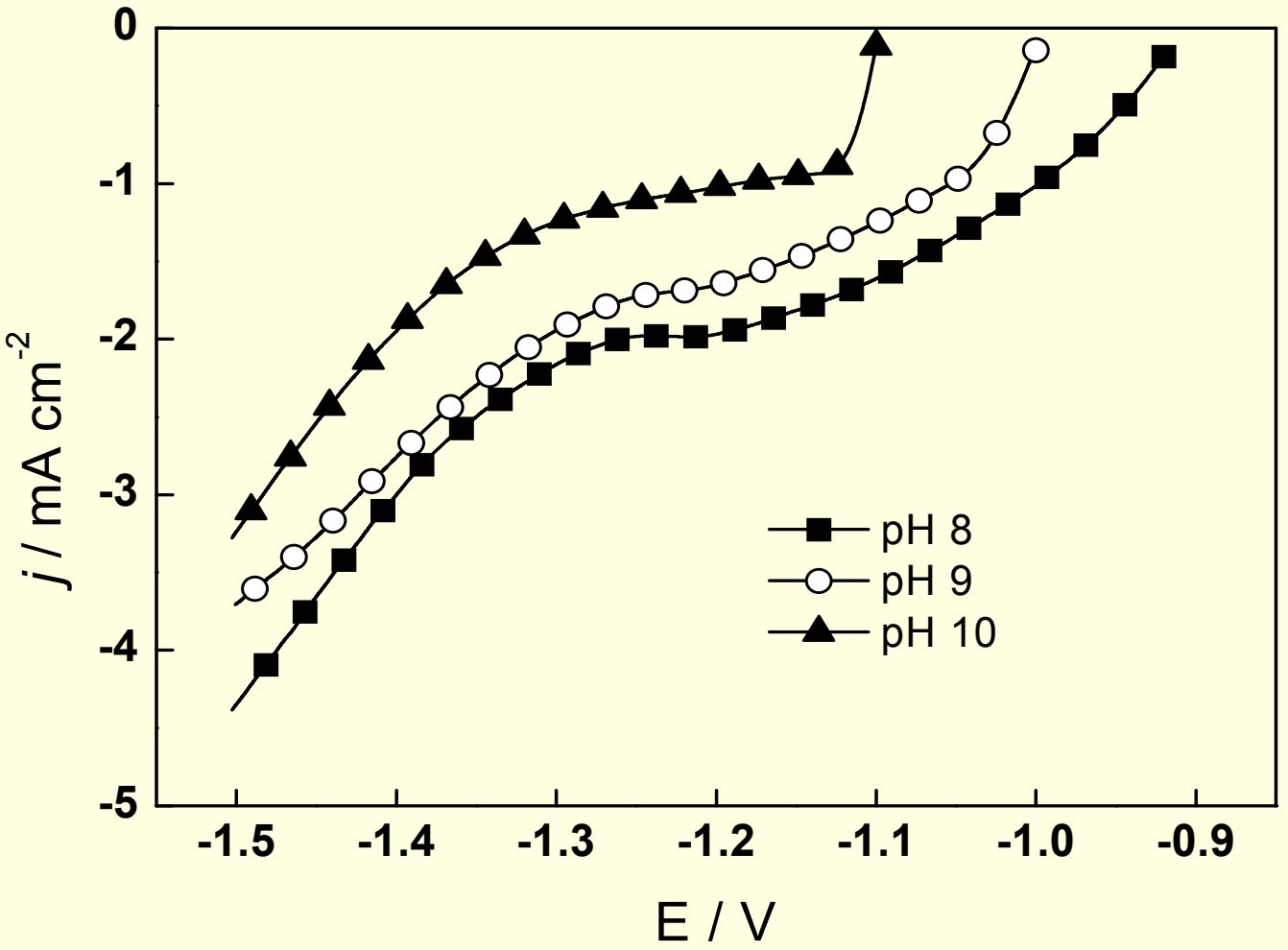
Experimental

- Working electrodes → Al (99.95%) foils with an exposed area of 8 cm^2
- A conventional three-electrode cell → a platinum mesh counter electrode, 3 M KCl/AgCl/Ag electrode as a reference (E = 0.201 V vs. SHE)
- Electroactive salt - $(NH_4)_6Mo_7O_{24}.4H_2O$ (0.0161 mol L^{-1}), pH of the electrolytes → NH_3-CH_3COONH_4 buffer solution
- The experiments → conducted at room temperature (22±2°C) in naturally aerated solutions
- The electrochemical behaviour of the oxides → characterized in a borate buffer solution (pH 7) prepared from 0.5 mol L^{-1} H_3BO_3 and 0.025 mol L^{-1} $Na_2B_4O_7.10H_2O$, 0.5 mol L^{-1} Na_2SO_4 added to increase electrolyte conductivity

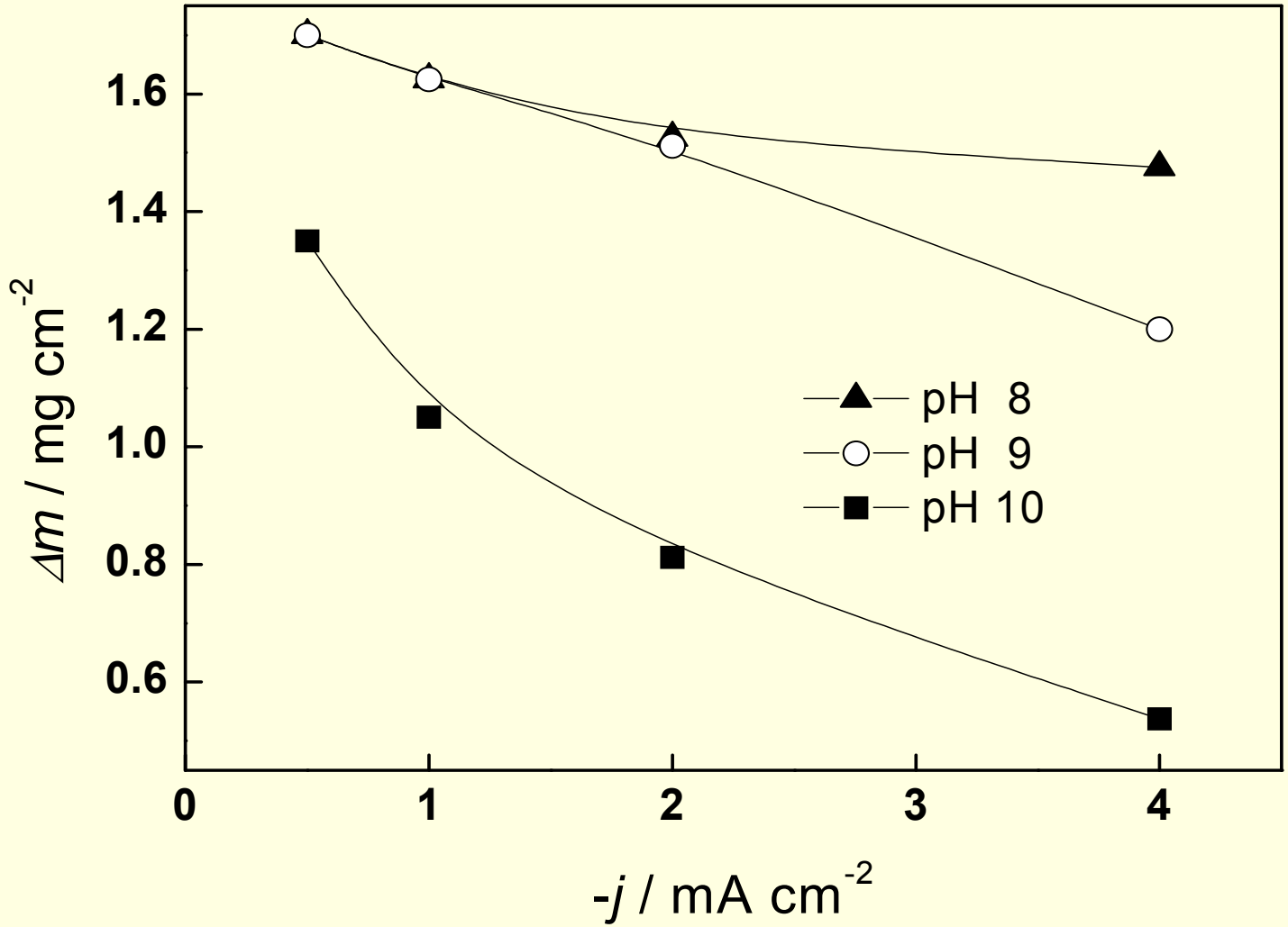
Apparatus and procedure

- Steady-state current-potential curves and electrochemical impedance spectra → Autolab PGSTAT 30/FRA2 (Eco Chemie, Netherlands)
- After reaching a stationary value of the current density at a constant potential → electrochemical impedance spectra in the frequency range 20 mHz to 51 kHz at an ac amplitude of 10 mV
- Reproducibility of the impedance spectra → ± 2% (by impedance magnitude) and ± 3º (by phase angle)
- Fitting and simulation of impedance spectra → Maple and Origin software
- X-ray photoelectron spectroscopy → Thermo Electron Escalab 250 spectrometer with monochromated Al Kα radiation (1486.6 eV)
- Fitting of the spectra → XPS Peak software

Current vs. potential curves

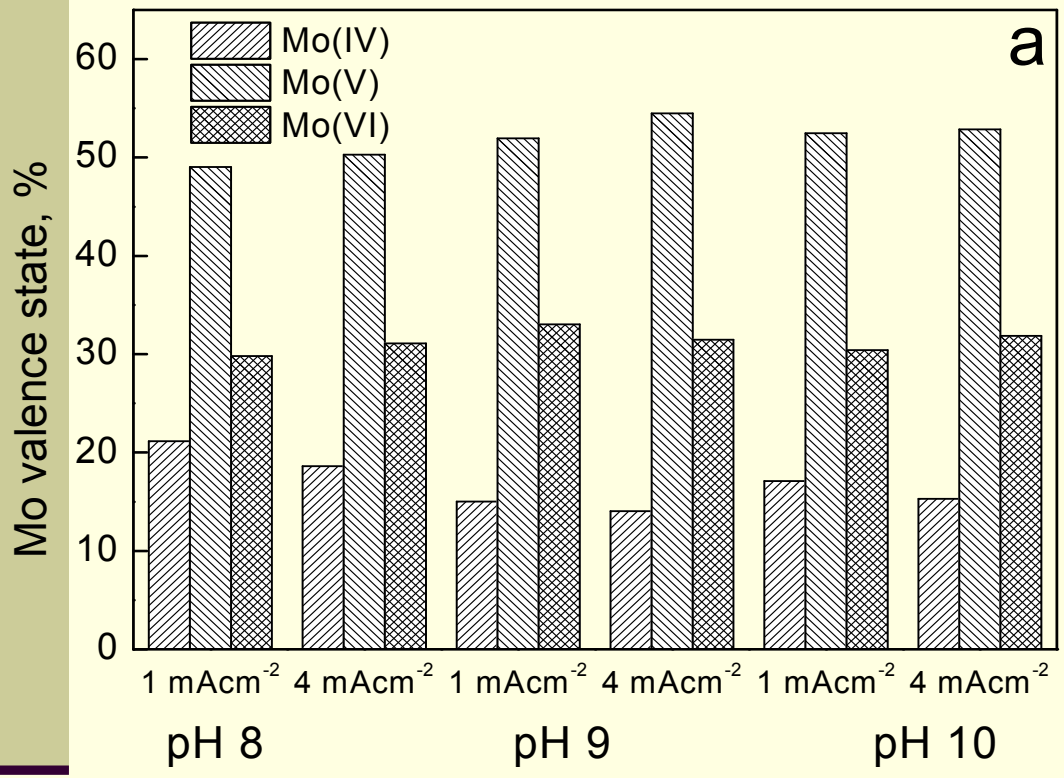


Dependence of the oxide weight on current density



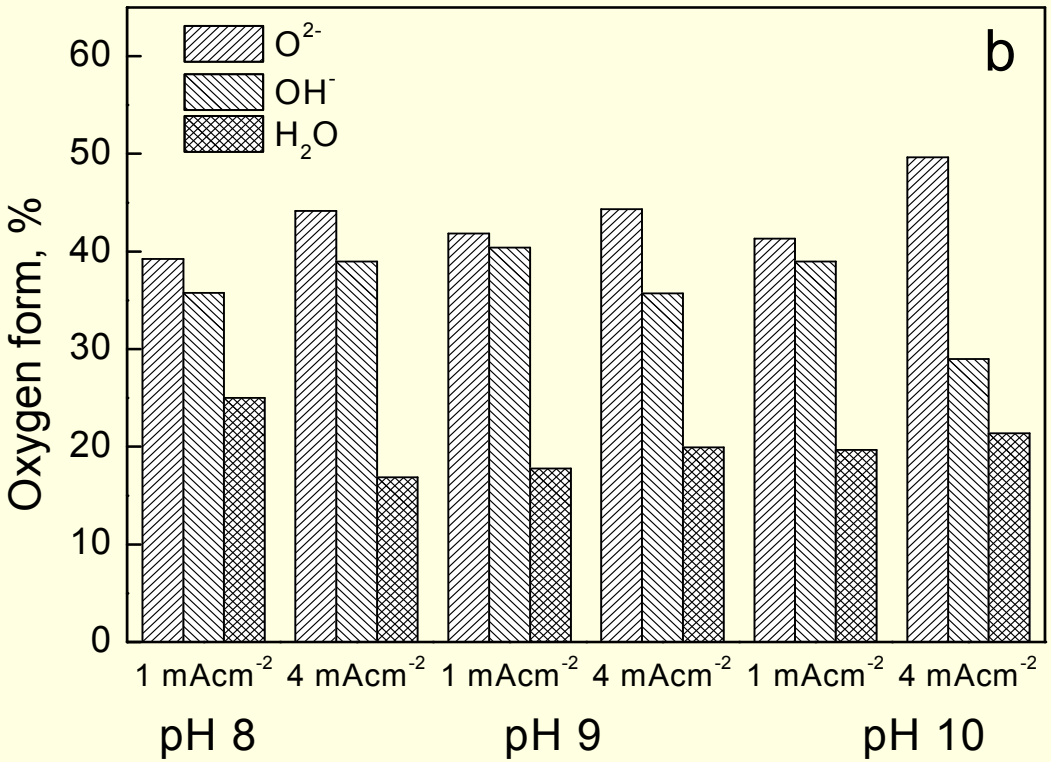
Constant charge – 2.4 C cm^{-2}

Composition of the oxides



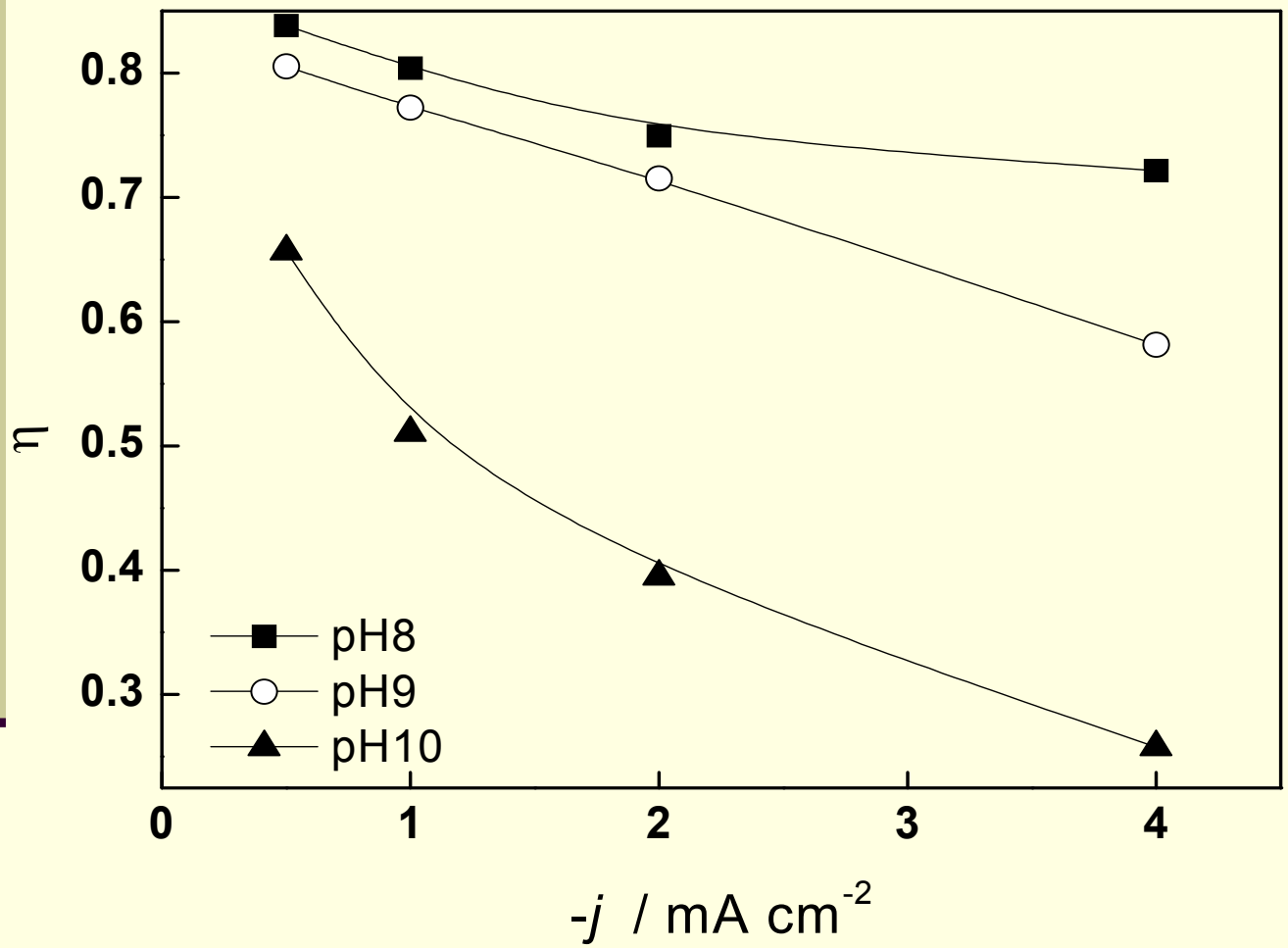
$$\frac{O}{Mo} = 1.80 - 1.86$$

$$\frac{OH}{Mo} = 1.4 - 1.7$$



$MoO_{1.8}(OH)_{1.5}(H_2O)_{0.8}$

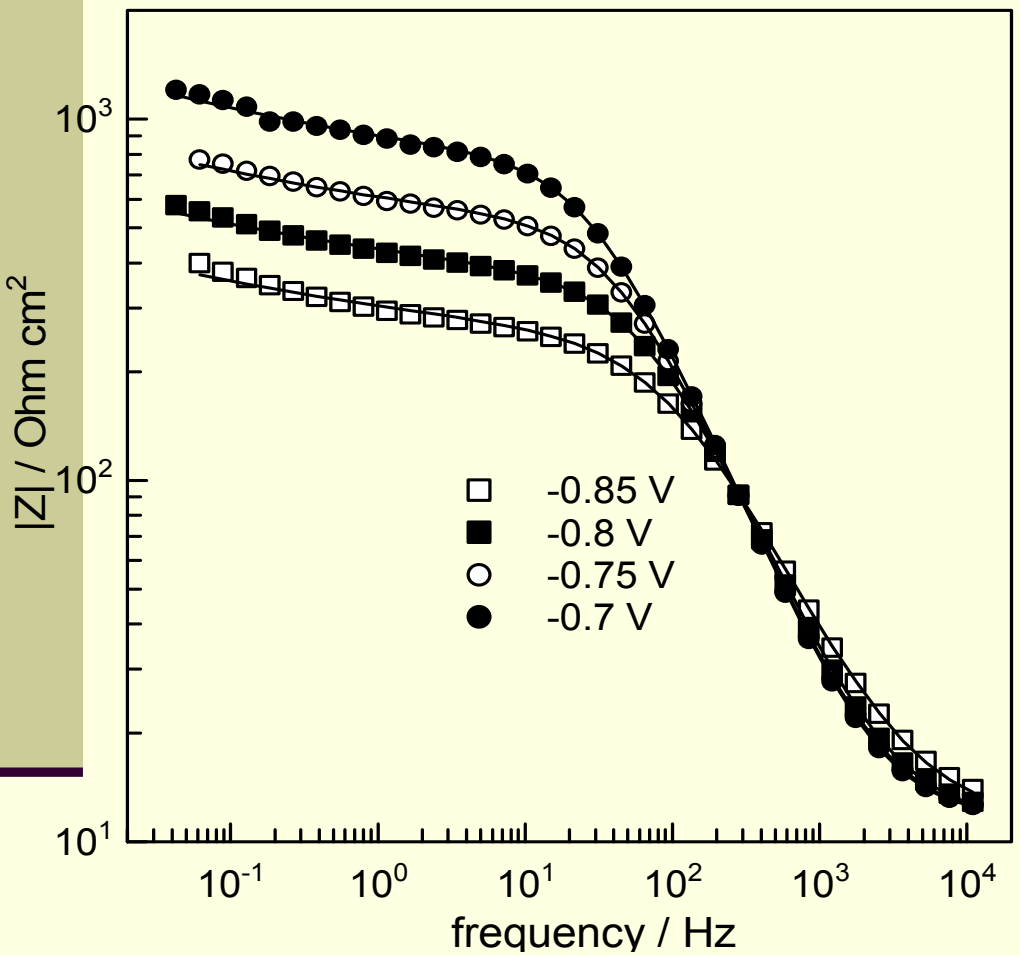
Current efficiency for deposition

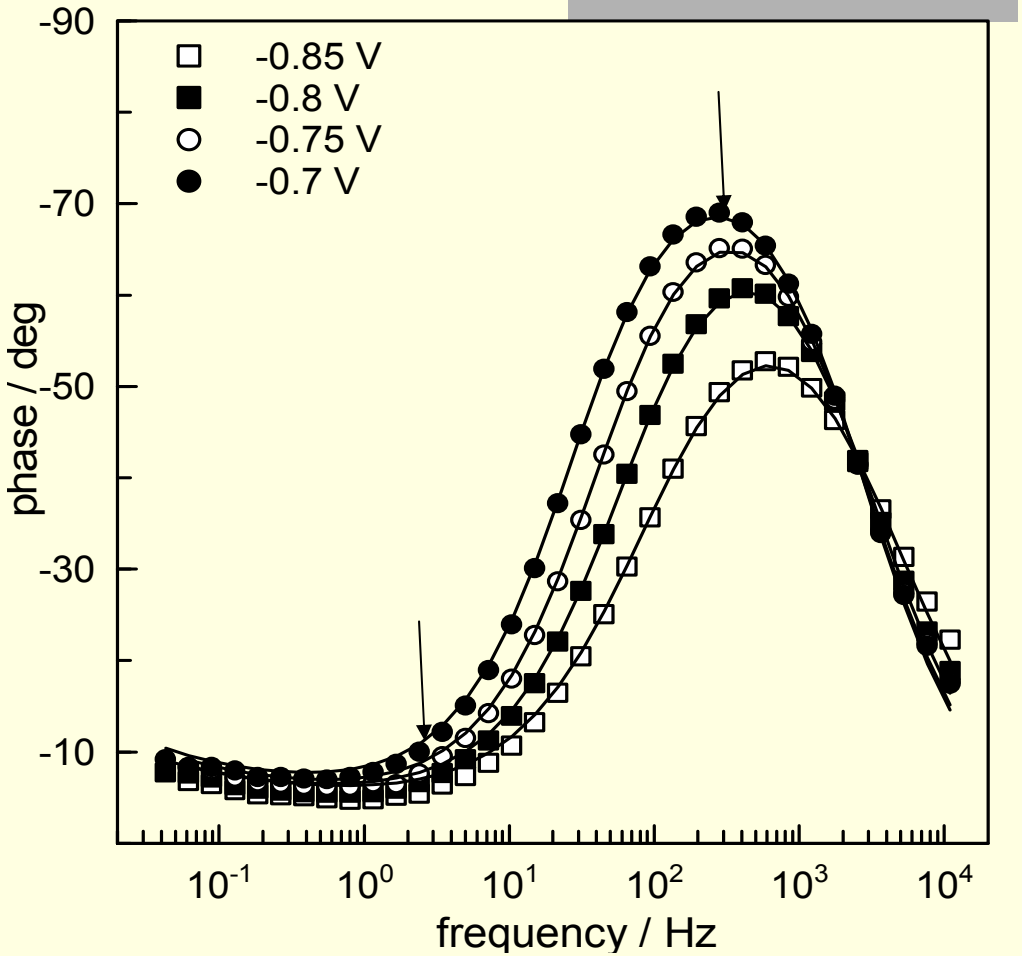


$$\eta = \frac{Q_{film}}{Q_{tot}}$$

Estimated mean thickness ~ 2.2–2.6 μm

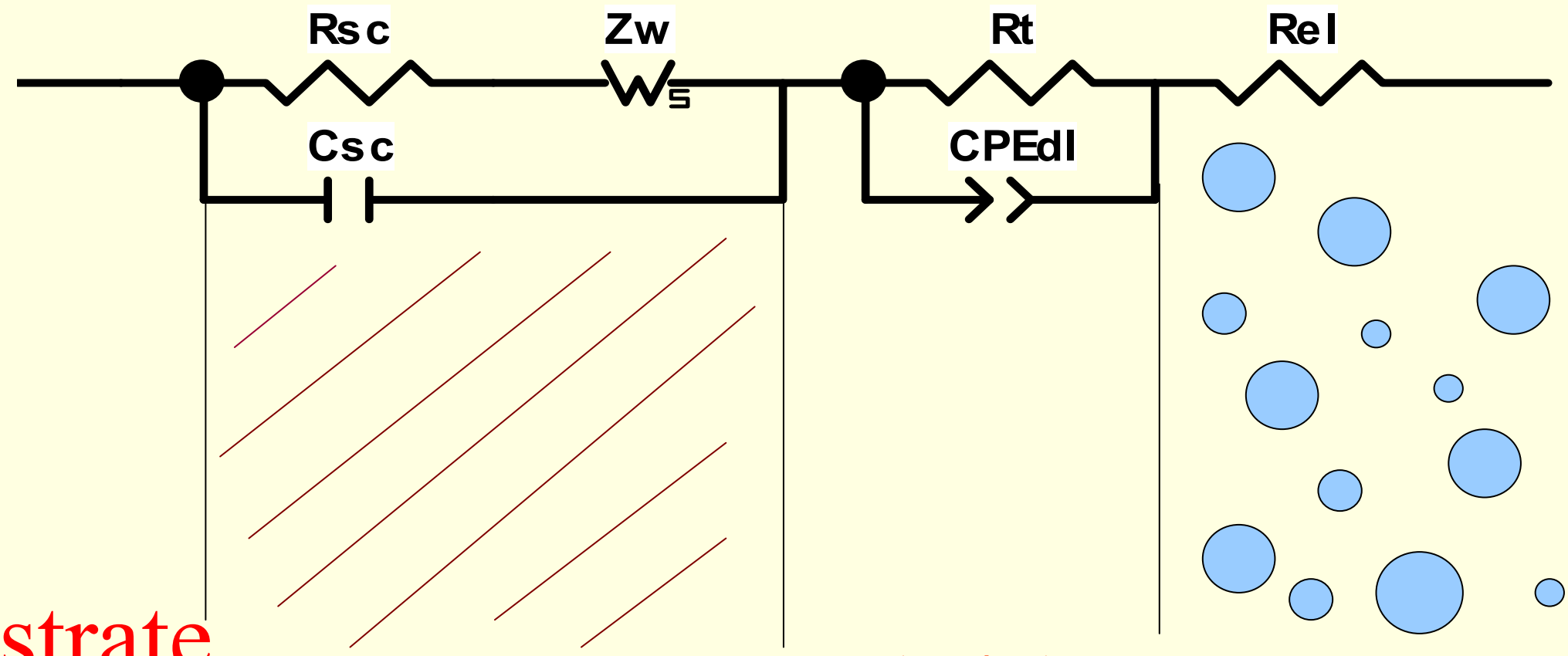
Anodic behaviour of electrodeposited oxides





pH 8, 0.5 mA cm^{-2}

Equivalent electrical circuit



substrate

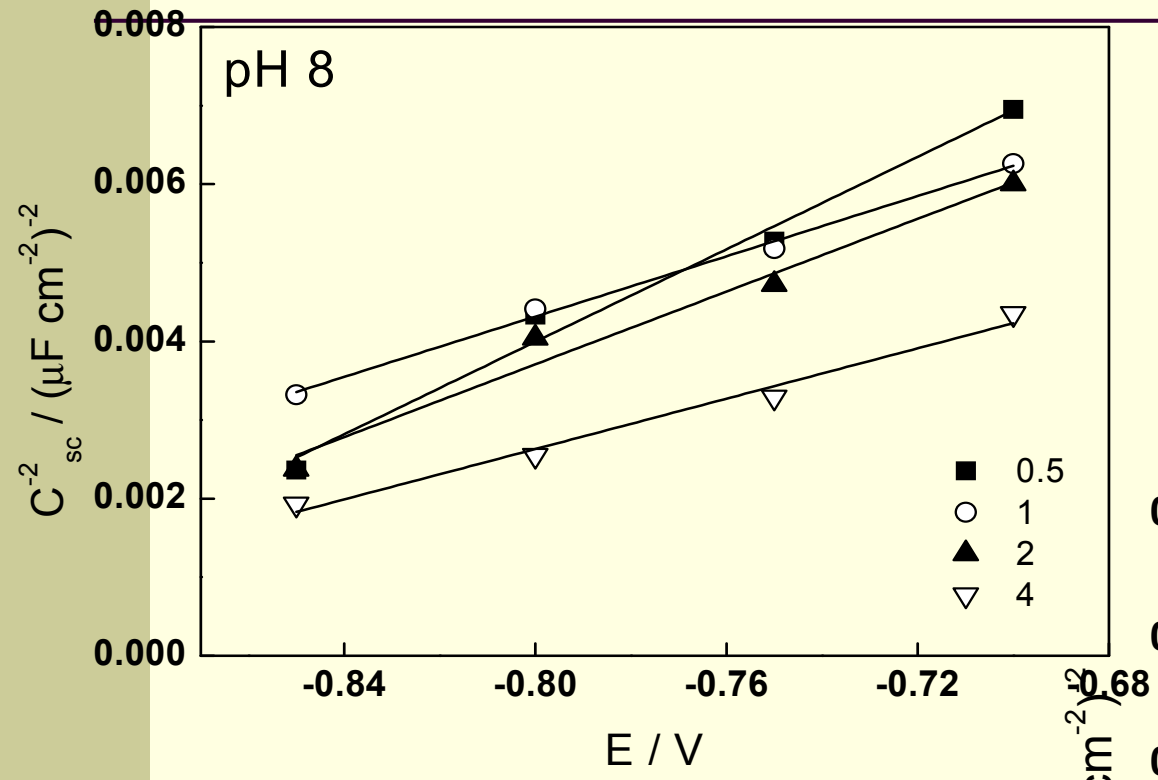
(M/F)

Film

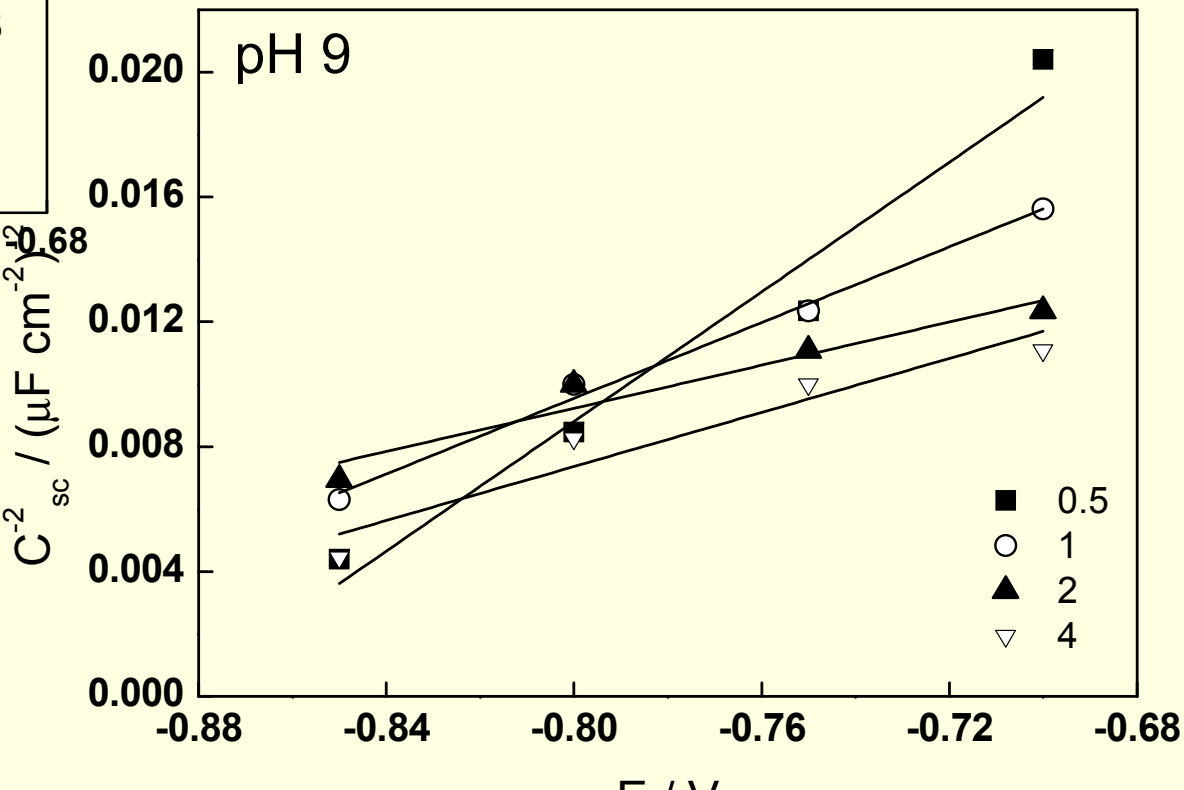
(F/S)

Electrolyte

Space charge layer capacitance



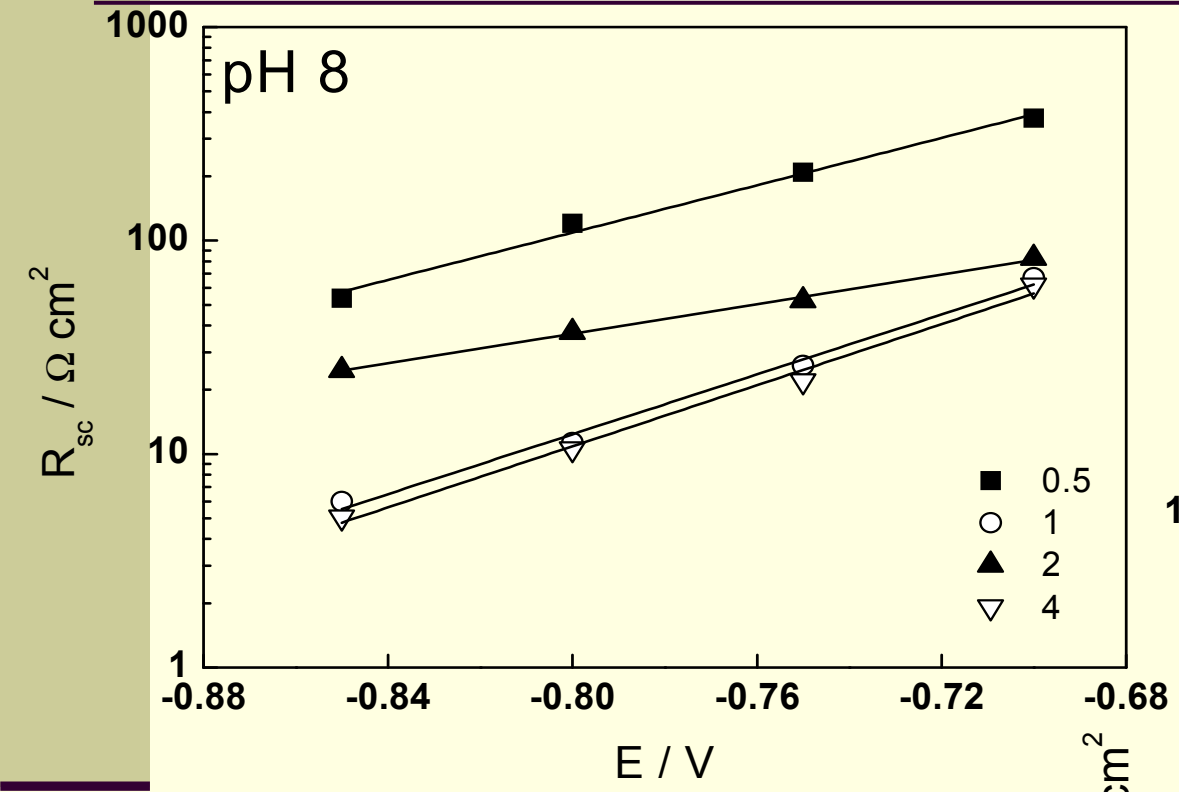
$$C_{sc}^{-2} = \frac{2}{e\varepsilon\varepsilon_0 N_D}(E - E_{fb})$$

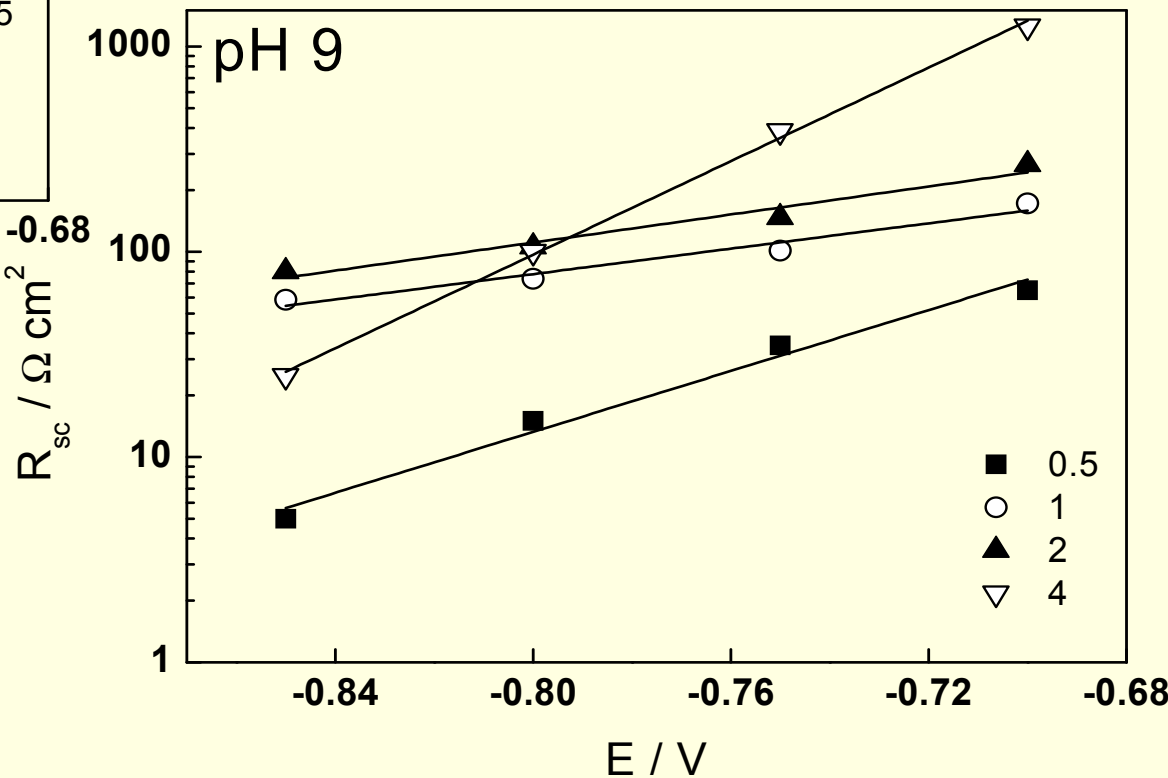


$$N_D \approx 0.5 - 3.0 \times 10^{20}\, cm^{-3}$$

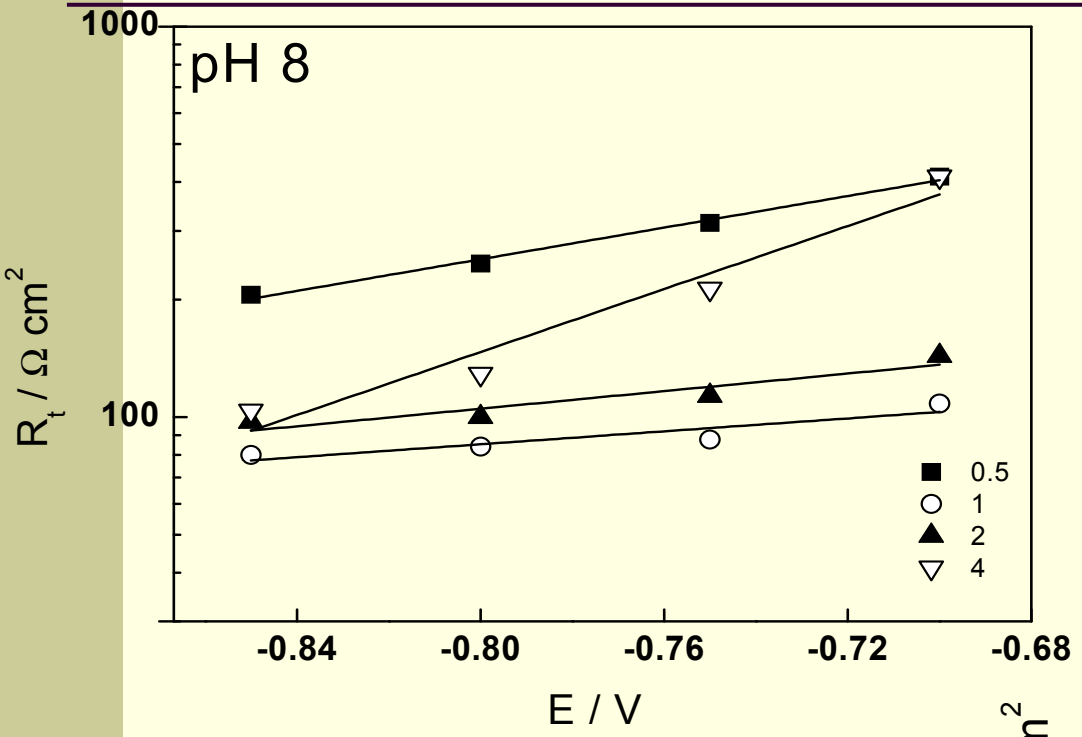
$$\varepsilon = 29.4$$

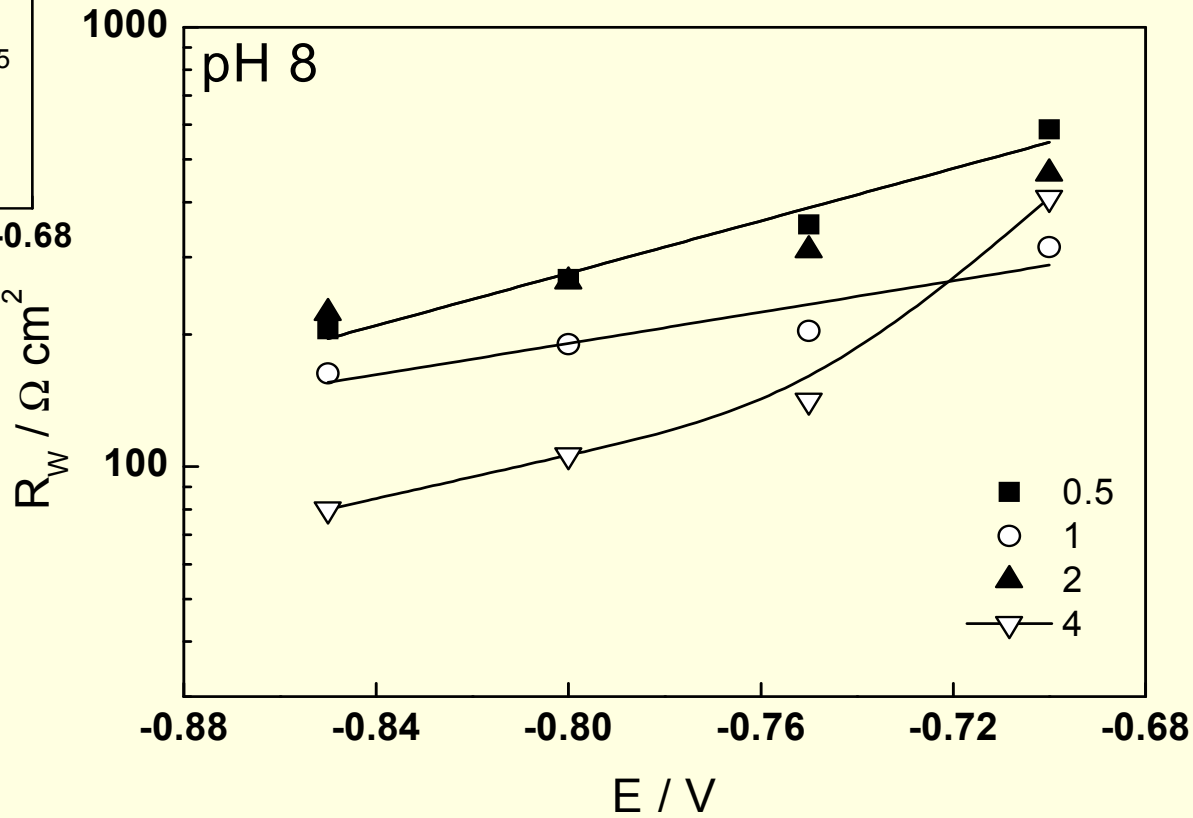
Space charge layer resistance



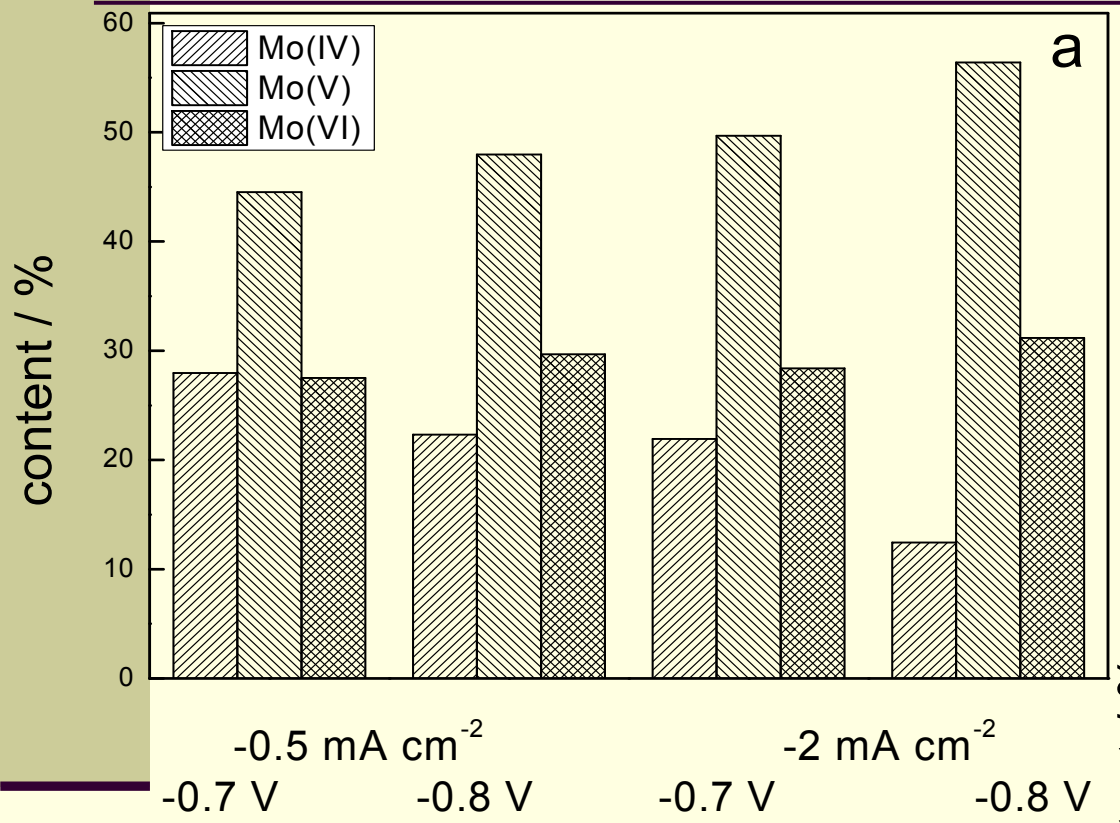


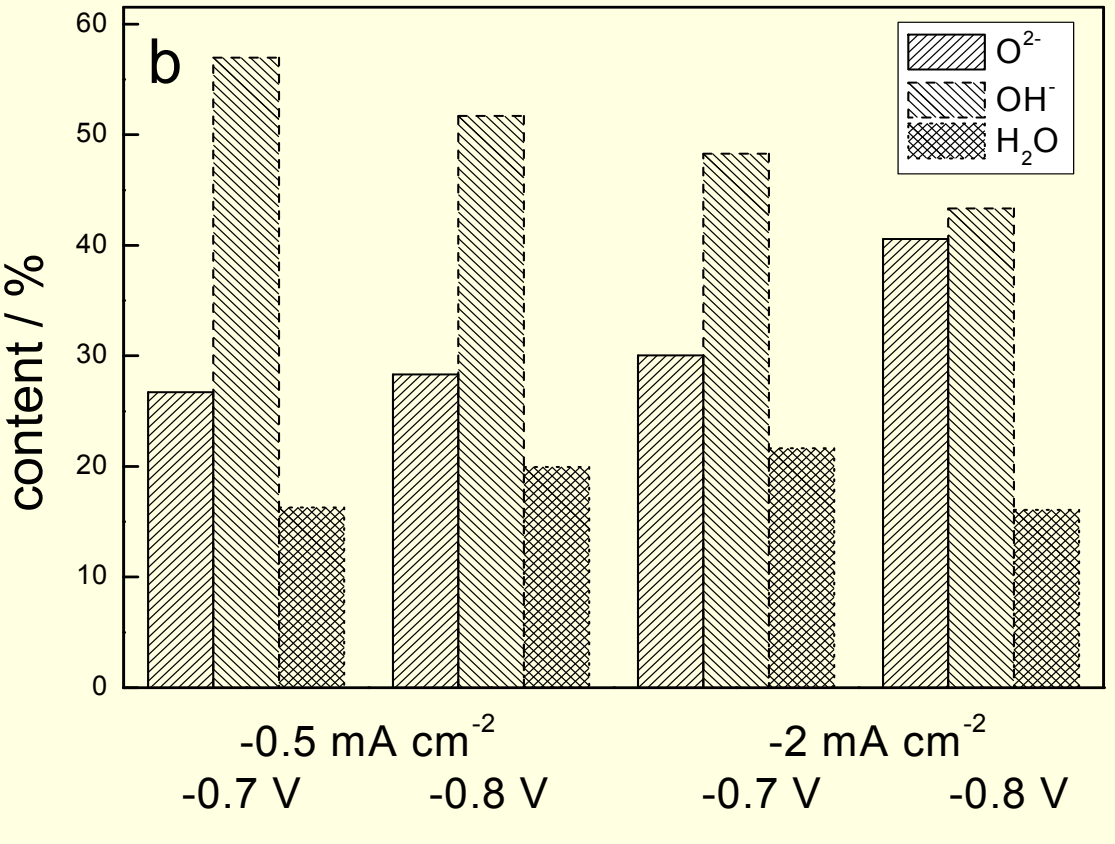
Charge transfer and ionic transport resistances





Composition of oxides after anodic polarization





Conclusions

- At least two processes can be detected in the investigated range of potentials, the process at less negative potentials being related mainly to the deposition of molybdenum oxides, whereas at more negative potentials, water reduction with hydrogen evolution starts to contribute to the overall current

- The current efficiency for film formation at constant charge decreases with increasing pH and the deposition current density. The decrease of the efficiency with increasing current density is the higher, the higher the solution pH. Accordingly, it reaches values close to 0.85 for films deposited from a pH 8 solution at 0.5 mA cm^{-2}

Conclusions (cont.)

- XPS analysis of films formed at constant charge in all the investigated solutions at low and high current densities demonstrate that the film is composed of Mo(IV) (13–20%), Mo (V) (ca. 50%) and Mo (VI) (ca. 30%) oxide/hydroxide. Evaluation of the concentration ratios between O bonded as oxide, hydroxide and water and Mo indicates a tentative composition of the surface oxide as $MoO_{1.8}(OH)_{1.5}(H_2O)_{0.8}$.

- Upon polarisation at potentials less negative than the open-circuit potential in a pH 7 borate buffer solution, the electrodes behave as mixed conductors, the electrochemical impedance spectroscopic evidence pointing to a formation of a thin n-type semiconductor barrier impeding the anodic charge transfer at the film/solution interface.

Thank you for your attention