Passive TiO_2 growth studies using Medium Energy Ion Scattering and Nuclear Reaction Profiling

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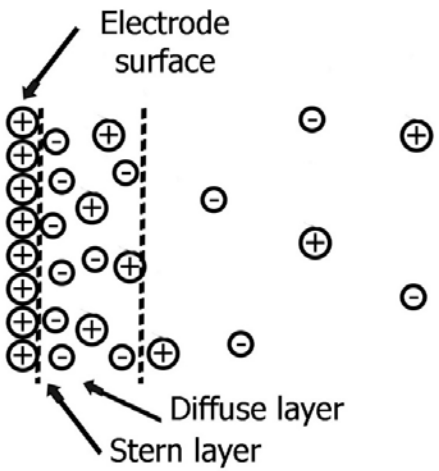
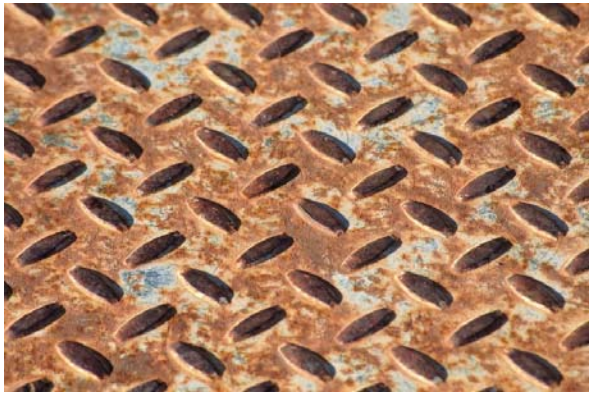
Introduction

- Adsorption/desorption at the electrochemical interfaces : fundamental and applied interest
- E.g. anodization
- Oxide layers: crucial for corrosion prevention
- E.g. Ti biomedical implants → anodization parameters → different film properties [1]→ Biocompatibility and adsorption from blood plasma [2]
- Develop techniques to study the oxidation at an atomistic level →develop better protective films
- **Goal**: Study migration of O species (molecular and ionic) in thin films

Anodization:



Passive oxides (rust) on metals:



[1] O.R. Camara, Electrochimica Acta 29 (1984) pp 1111-1117, [2] T.M. Yang, J. Biomed. Mater Res. 50 (200) pp 499-5119

Isotopic labeling procedure

- **Ti films deposited** on Si(001) by magnetron sputtering

- **Isotopic labeling:**

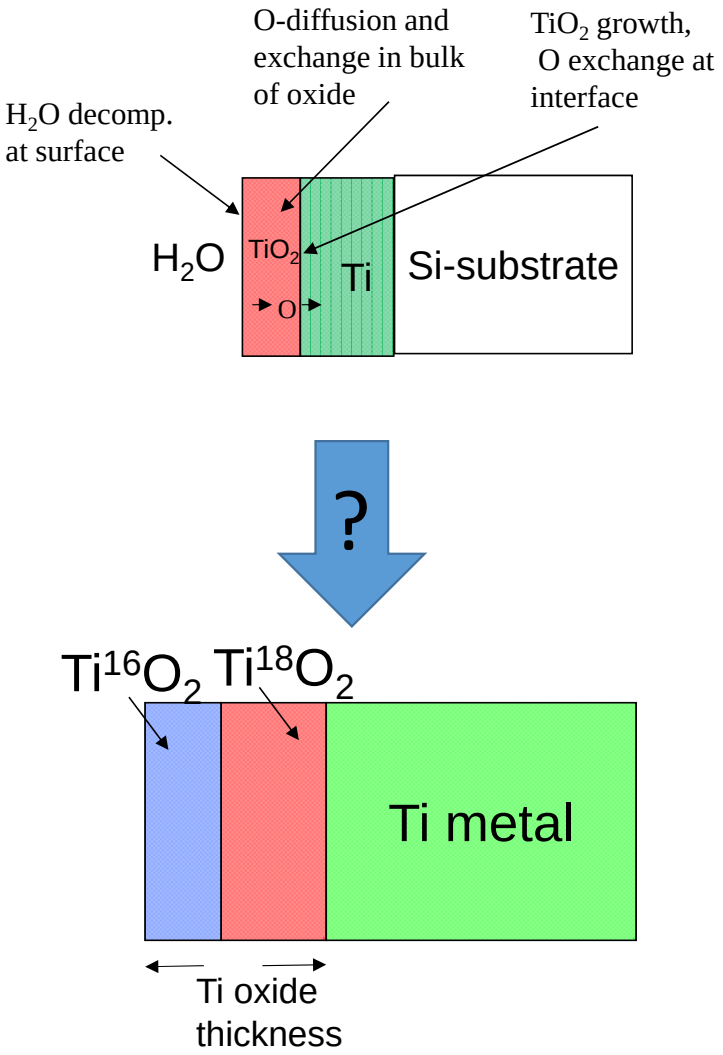
(1)Ti sample is exposed to isotopic (^{18}O) water: ultra thin TiO_2 film ≈10 nm

(2)TiO_2/Ti/Si(001) electrochemically oxidized in $H_2{}^{16}O$ water (voltages 0.0-10.0 V)

- **MEIS & NRA**:

-Depth profiles of elements throughout film

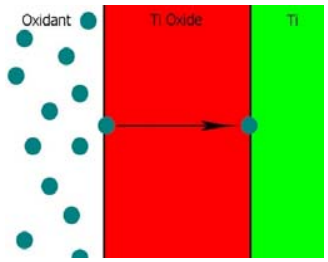
…Use depth profiles of O isotopes to infer principles governing oxidation!



Two major oxygen transport mechanisms

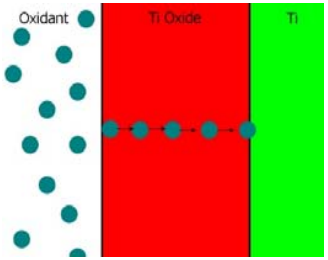
A

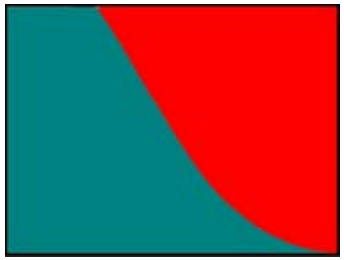
Interstitial O transport (no exchange) to interface



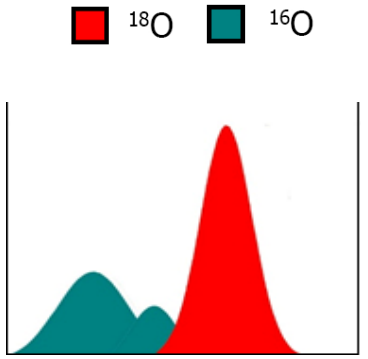
B

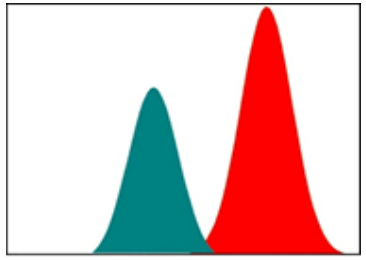
Oxygen vacancy transport





Concentration vs Depth



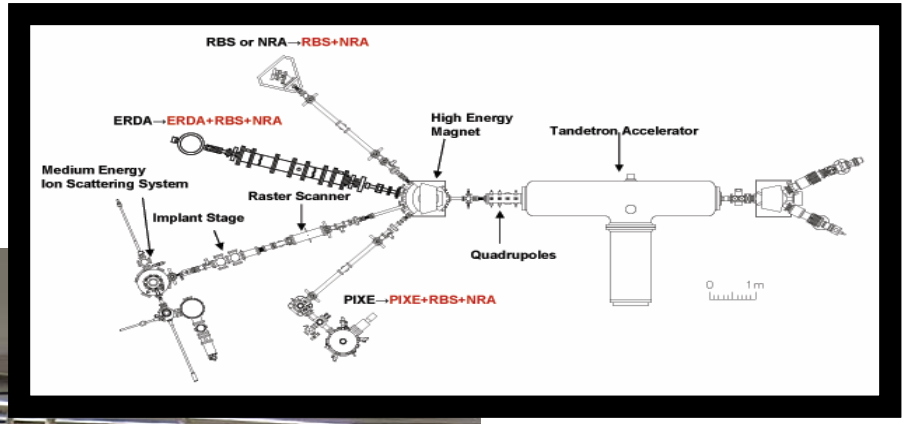


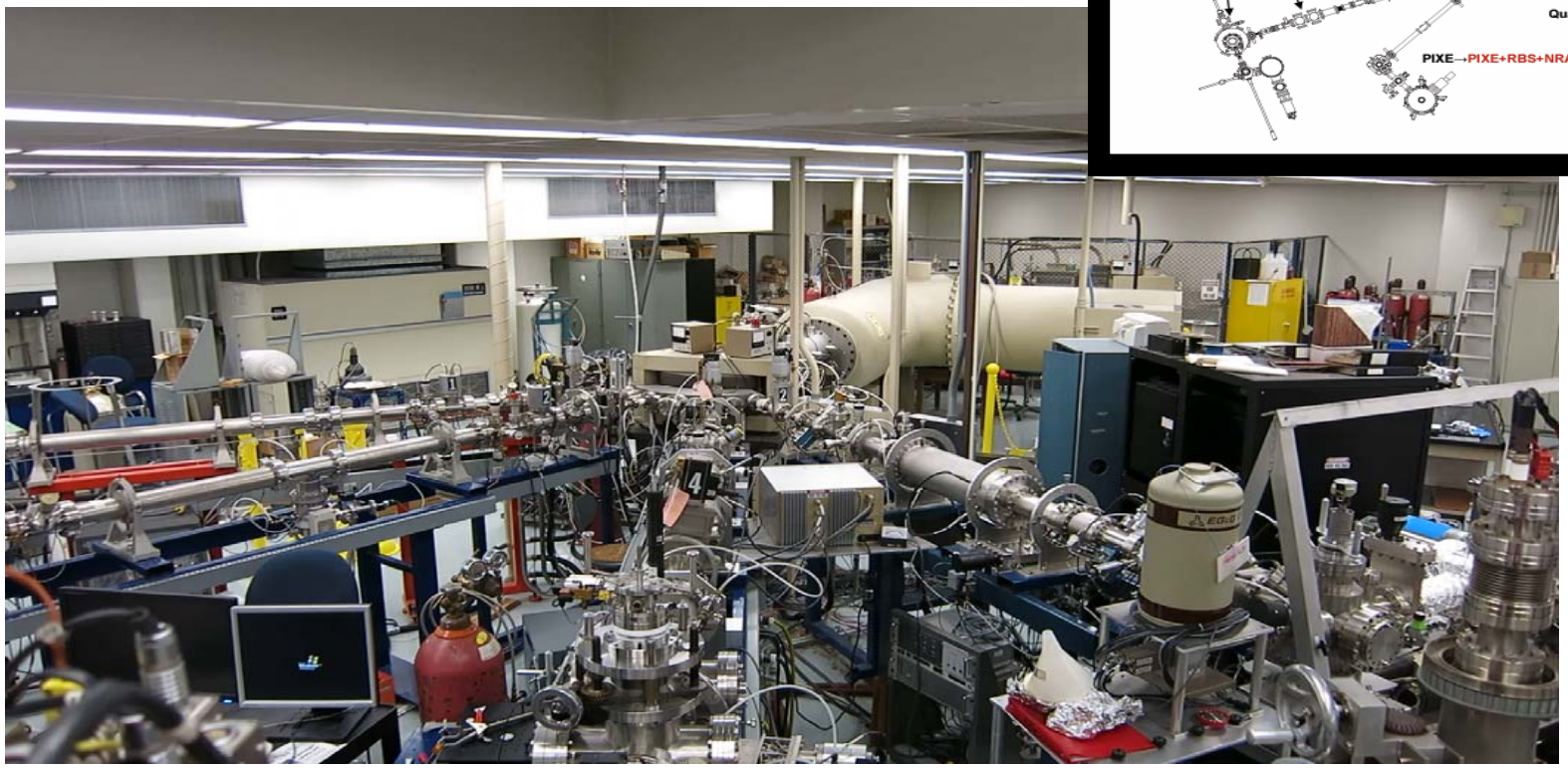
Ion Scattering Yield vs Energy

Case A: O is the mobile species and moves interstitially without reacting with the TiO_2 . New oxide forms at the oxide/metal interface

Case B: If O is the mobile species and there isotopic exchange, results in concentration profile for ^{16}O

1.7 MeV Tandetron Facility

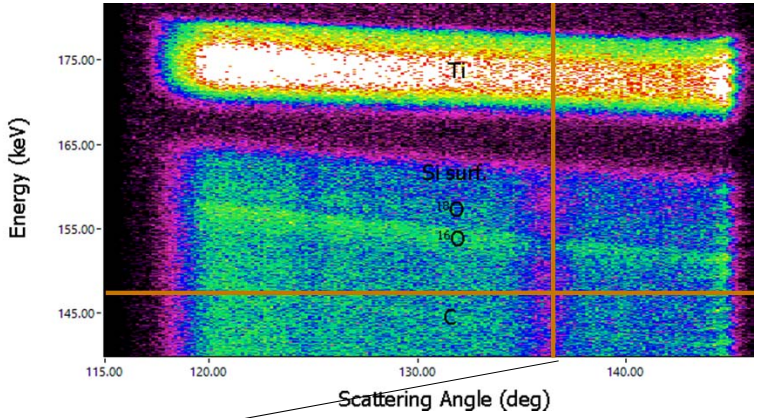




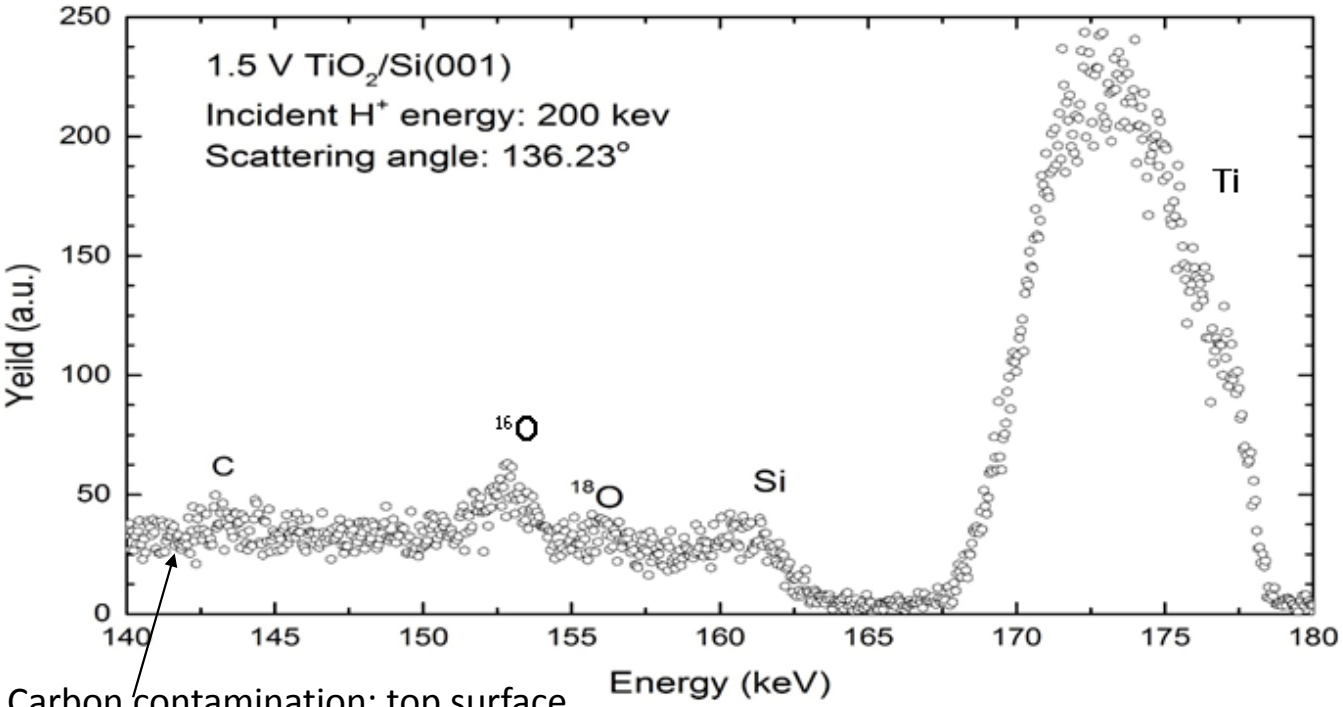
Beam-lines of Tandetron Accelerator Facility, Western Science Centre G49

MEIS Spectrum - TiO_2 Film

- MEIS spectra for TiO_2/Ti/Si(001) using 200 keV H^+
- Toroidal electrostatic analyzer (TEA)
- Scattering Intensity as function of angle at fixed energy



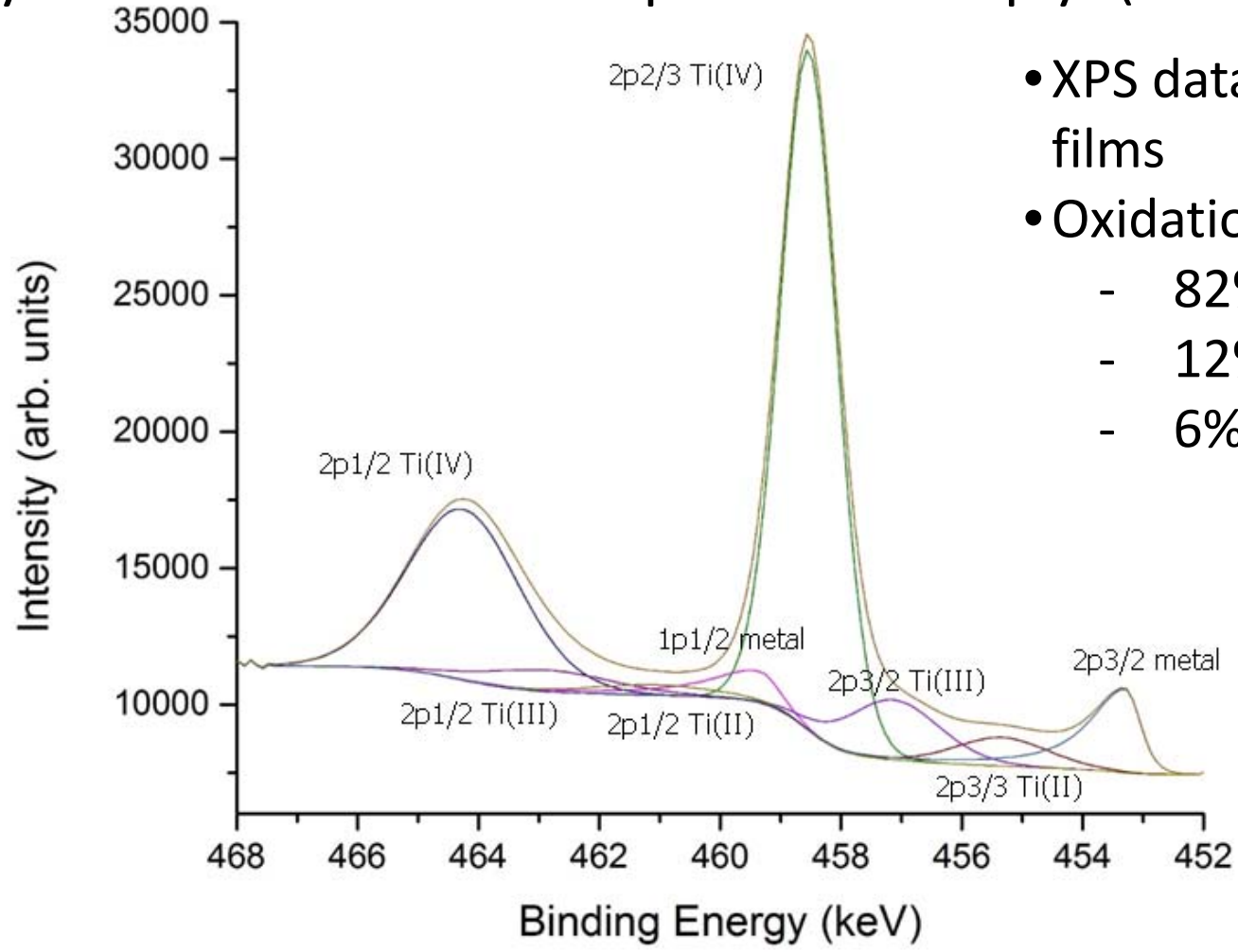
*Energy distribution for **one** angle*



Carbon contamination: top surface

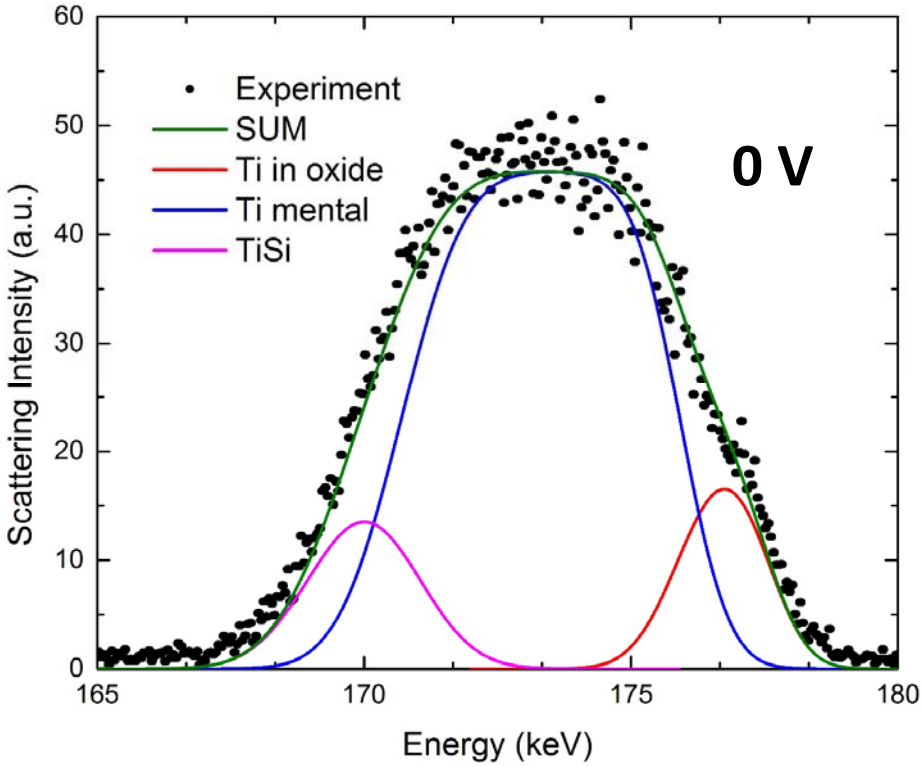
- O isotopes resolved, different kinematic factors
- Despite poor low-Z sensitivity
- Channelling and thin film thickness

X-Ray Photoelectron Spectroscopy (XPS)



- XPS data of TiO2 thin films
- Oxidation state (in oxide):
  - 82% Ti (IV)
  - 12% Ti (III)
  - 6% Ti (II)

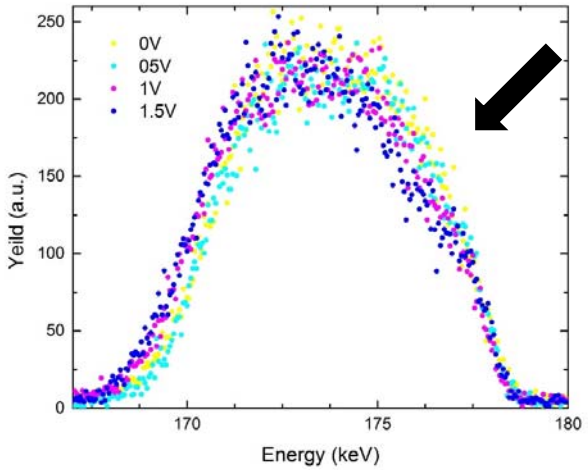
Variation in Ti Features

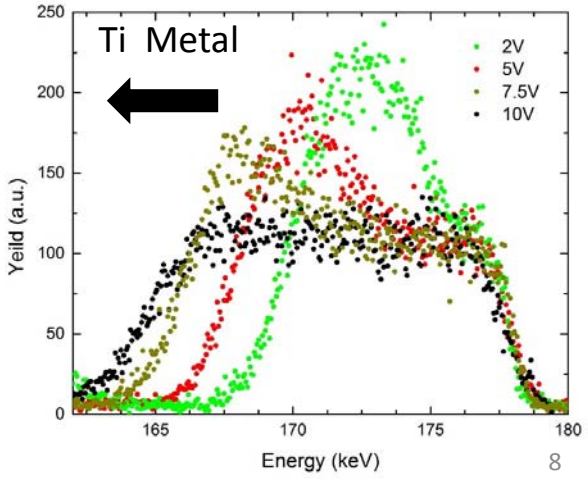


- Experimental Data: Ti and TiO2 as function of voltage
- Oxide growth: not limited to exchange reactions

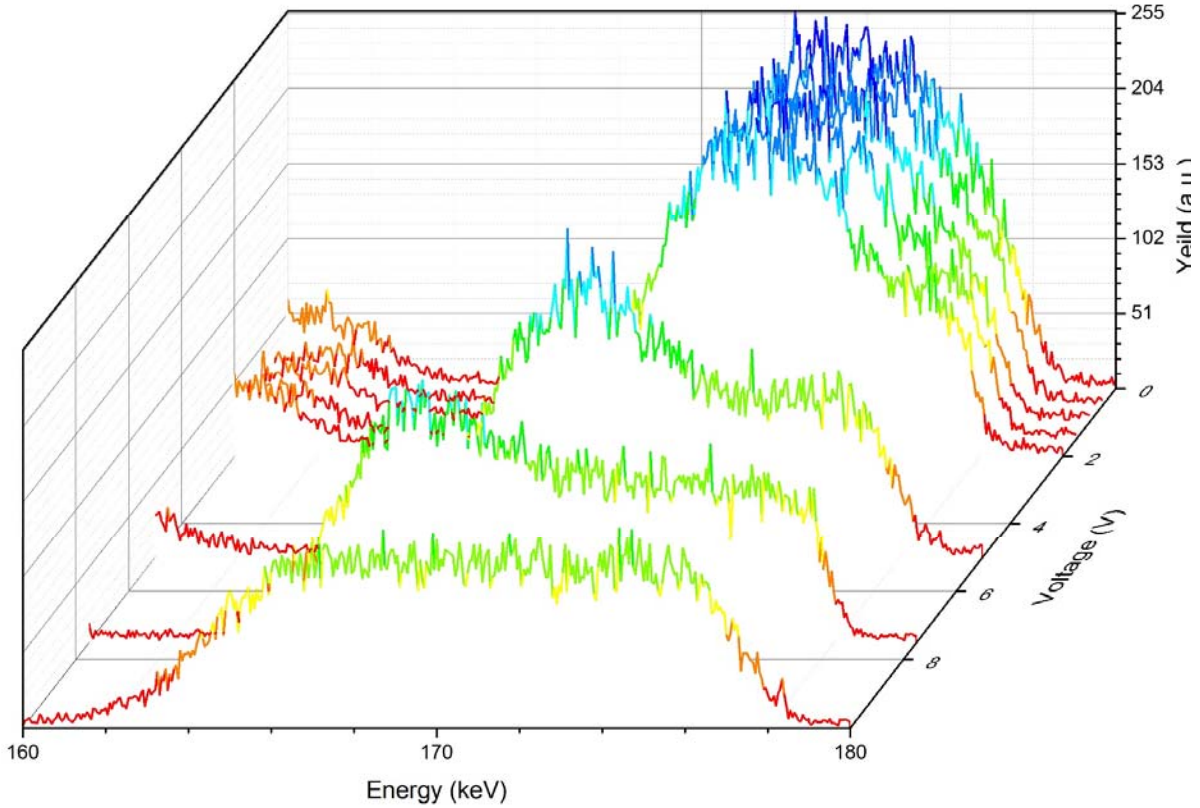
Oxide growth:

Ti in Oxide





Variation in Ti Features



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Oxide growth:

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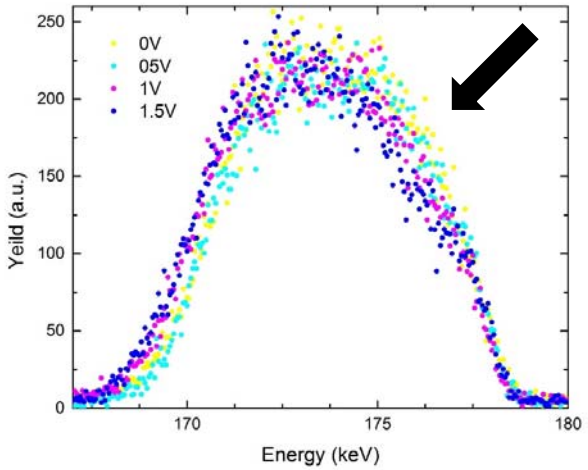
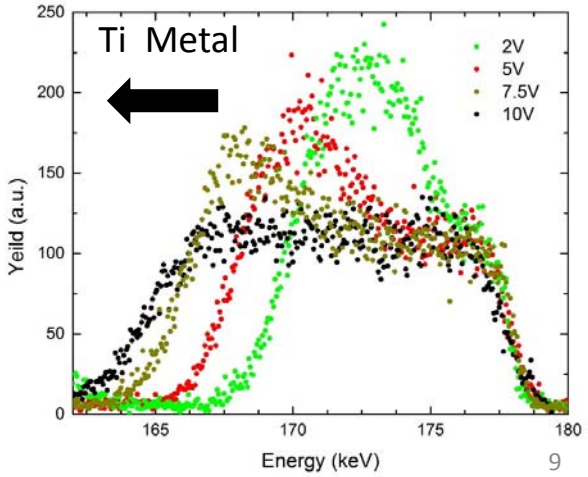
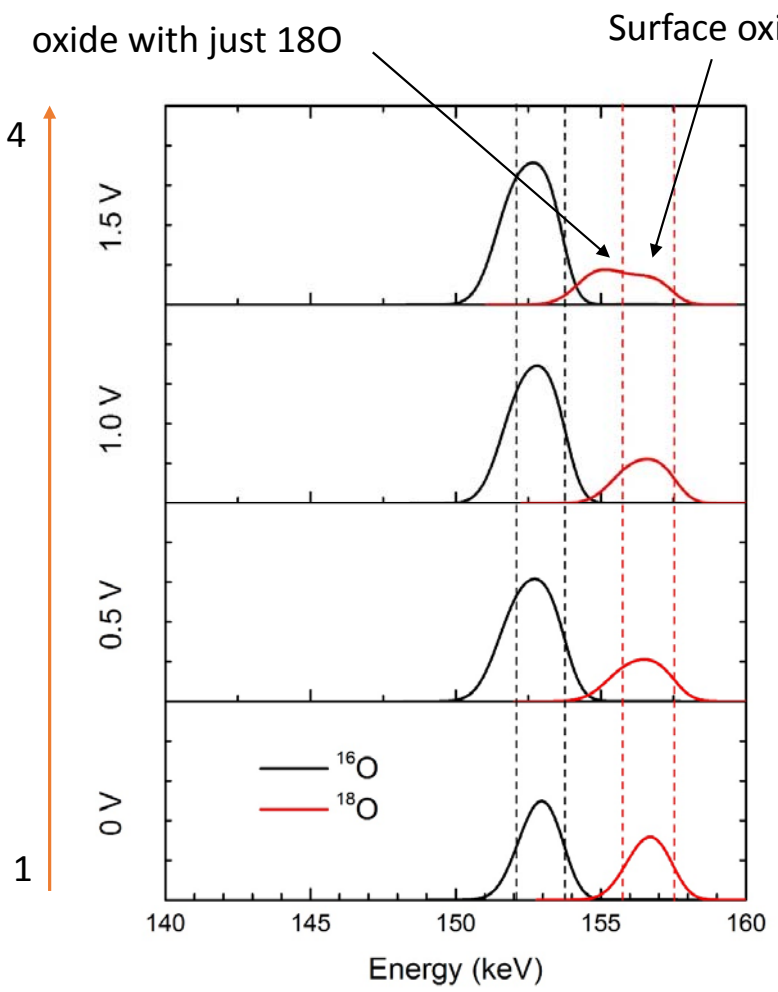
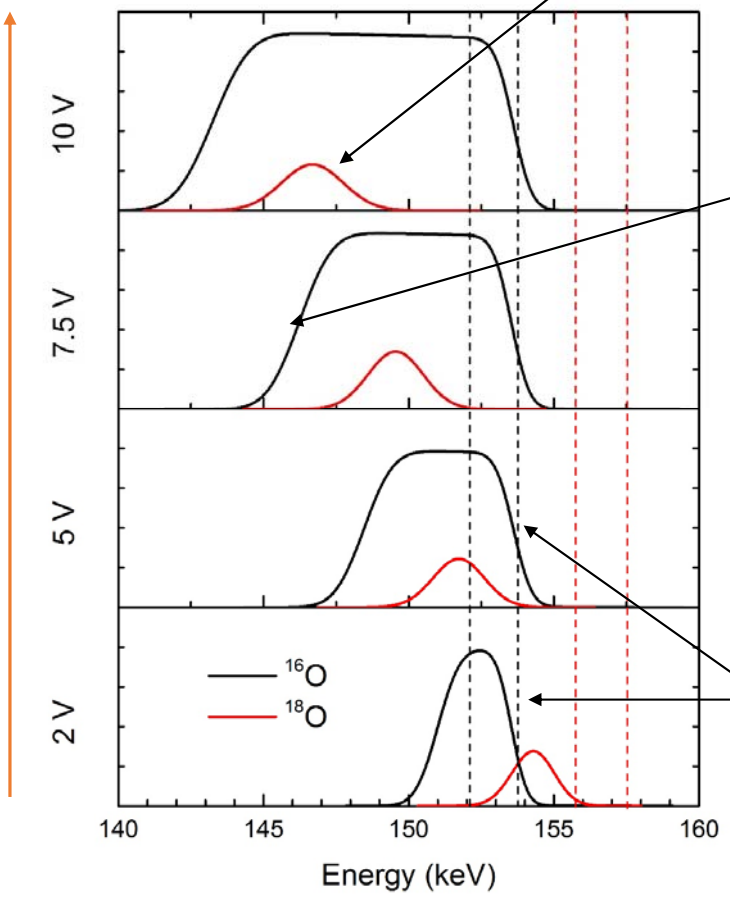




Variation in O Features

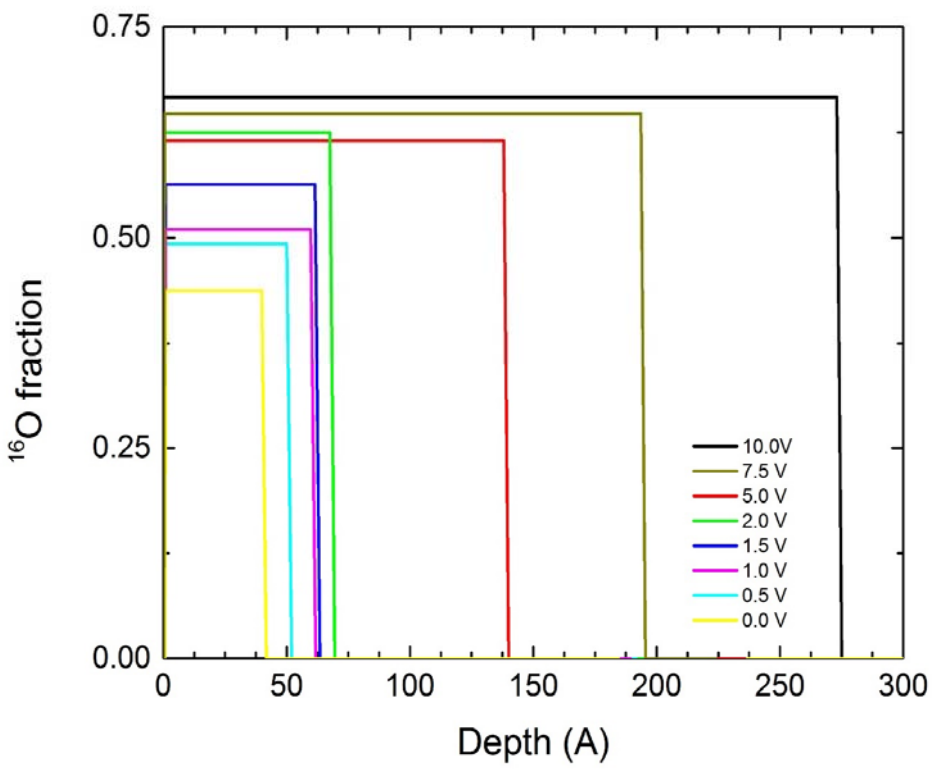
- Constant 18O
- 18O peak moves to increasingly lower energy

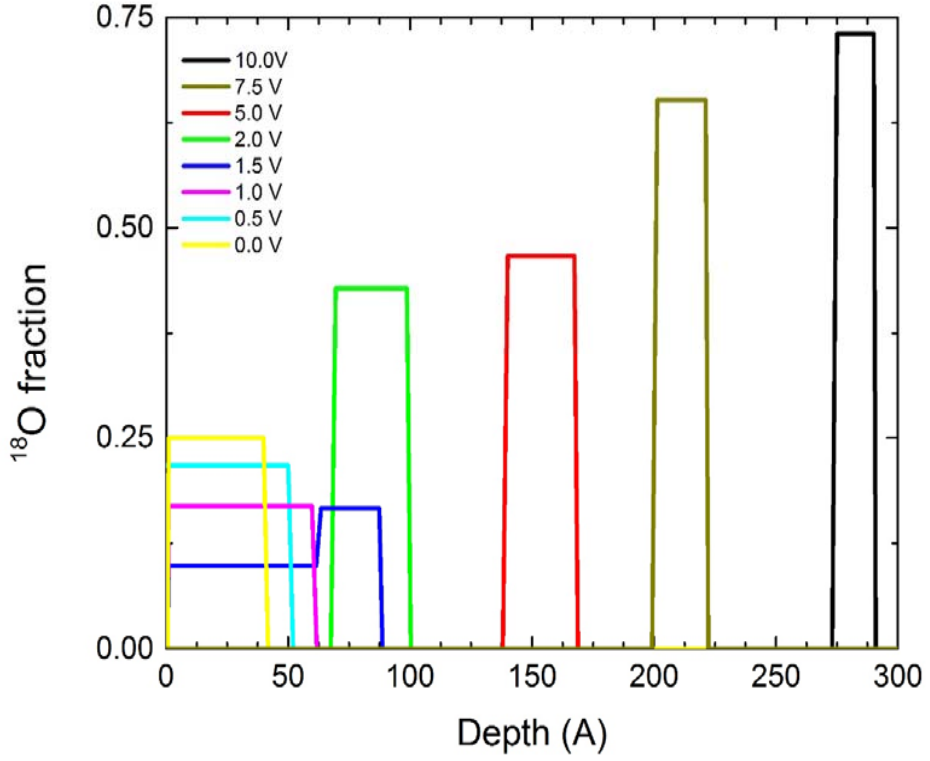




- 16O transported from electrolyte/oxide interface through bulk of oxide
- Lack of O “mixing”: exchange reactions
- New Oxide growth from ^{16}O incorporation at electrolyte/oxide interface

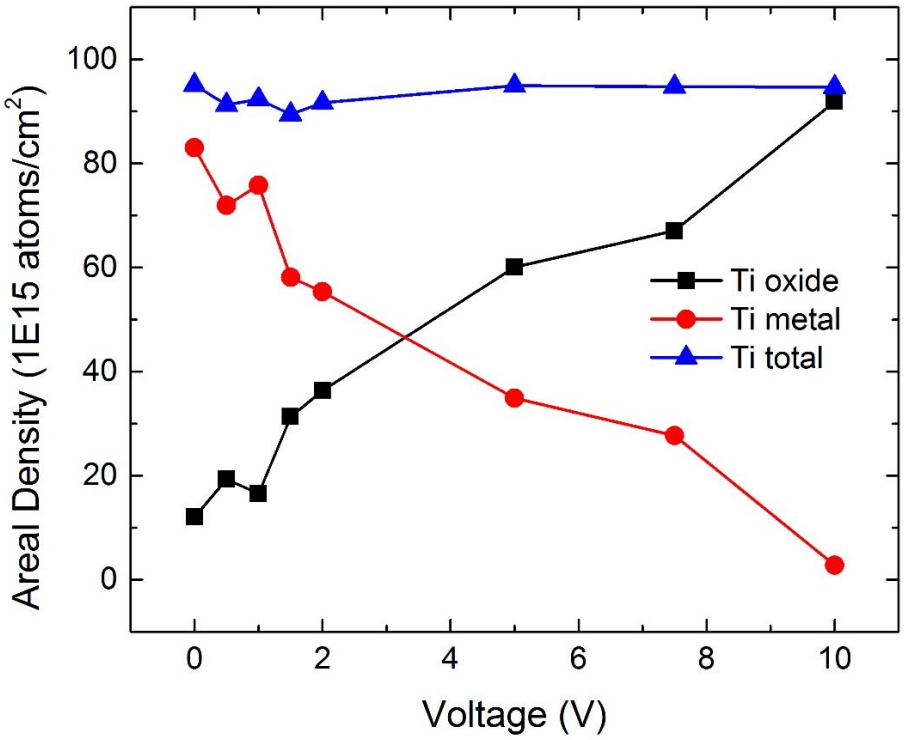
^{16}O & ^{18}O isotopic depth profiles

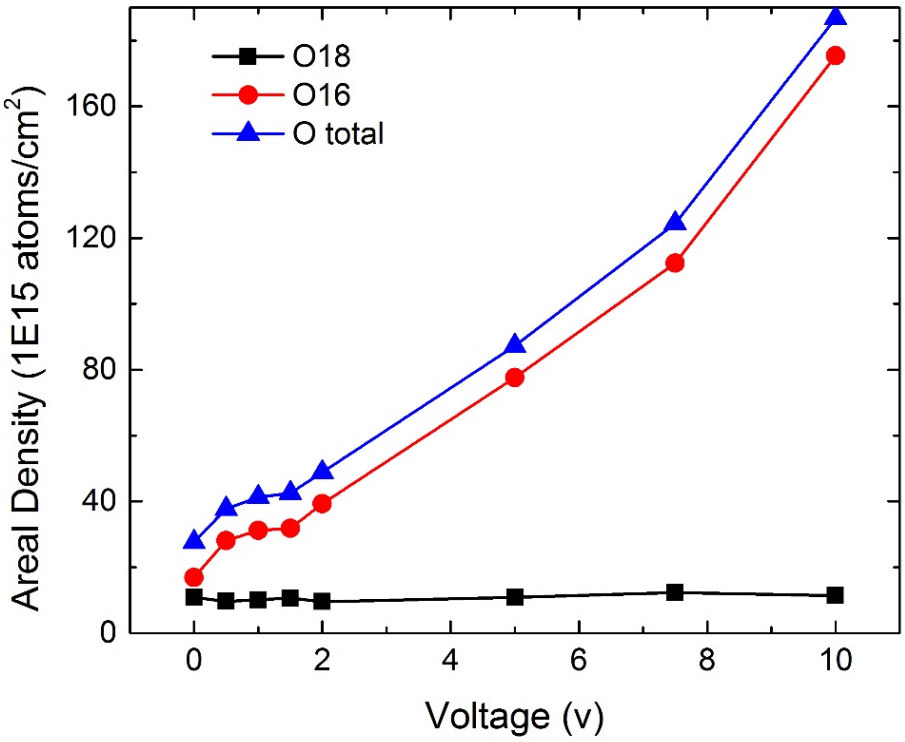




- Depth profiles used to simulated H+ MEIS experimental data
- Oxide growth as a function of voltage

Summary of MEIS

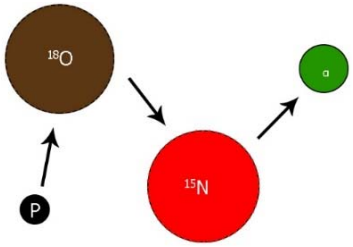




- No Ti lost to liquid phase
- Amount of Ti in oxide form increases as function of voltage
- Commensurately, quantity of Ti metal decreases

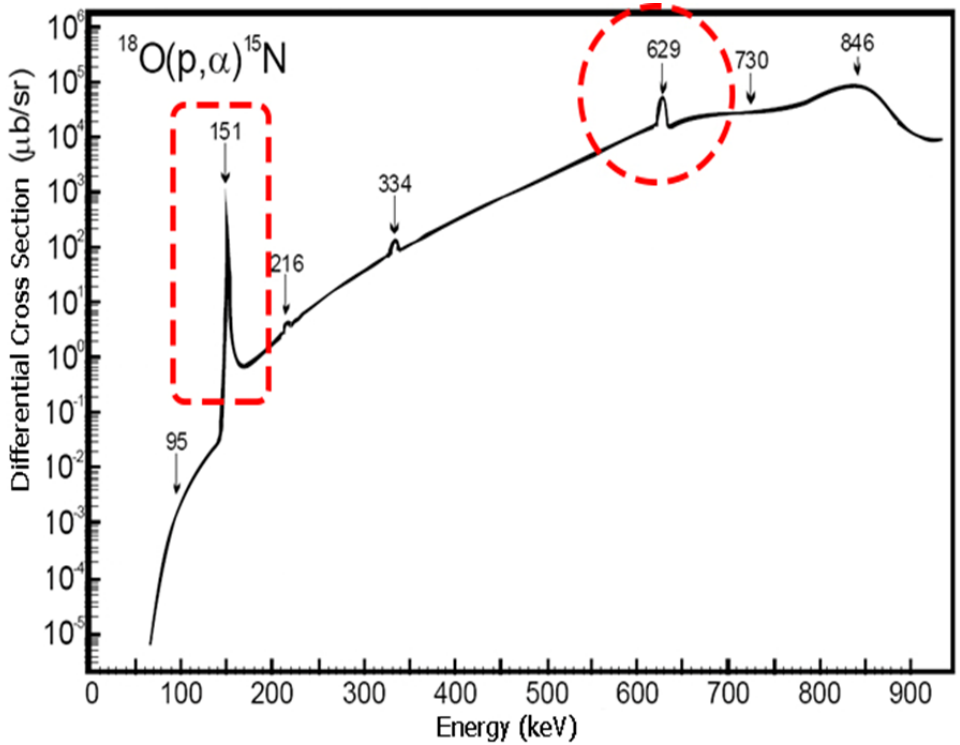
- New Oxide growth from ^{16}O incorporation
- Isotopic exchange at electrolyte/oxide interface
- ^{18}O transport to oxide/metal interface

Nuclear Reaction Analysis (NRA): ^{18}O (p, α) ^{15}N



Resonance	Width	Depth Resolution
151 keV	.05 keV	High
629 keV	2.1 keV	Low

properties of the two resonances [1]



Differential cross sections for the ^{18}O (p, α) ^{15}N reaction. Note the narrow width of 151 keV. DCS decrease by several orders of magnitude [2]

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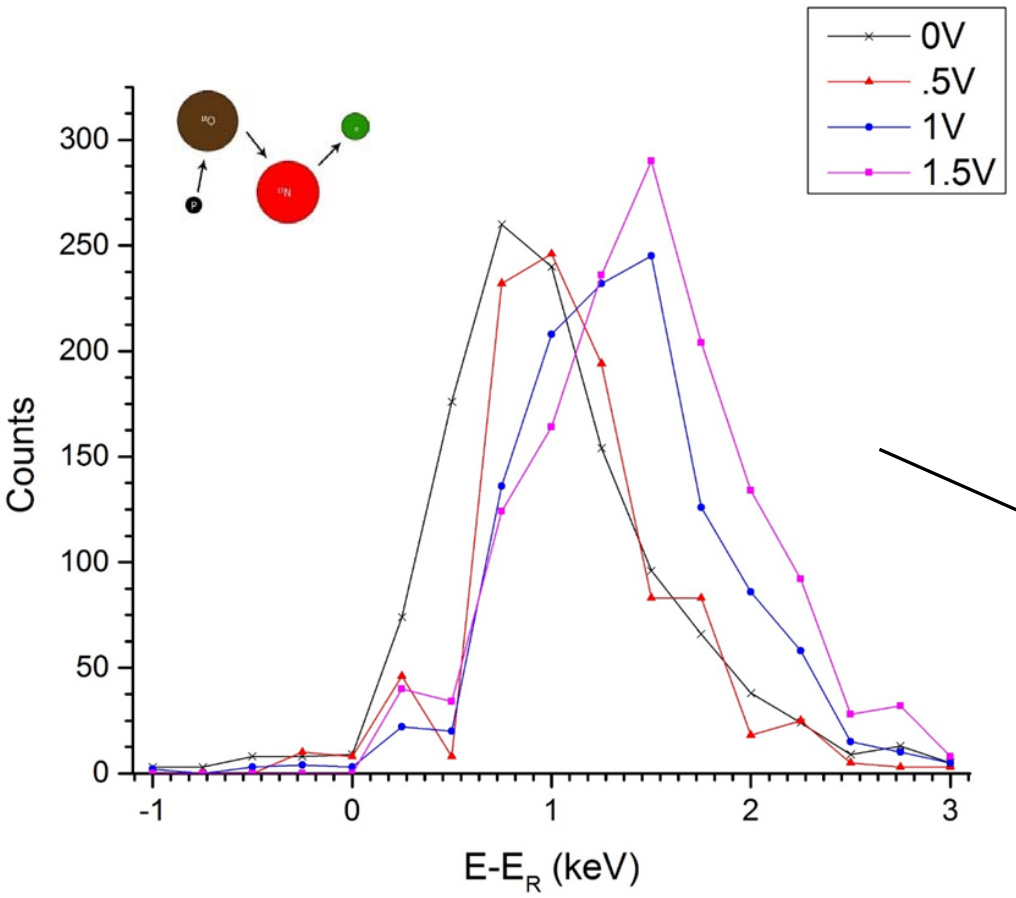
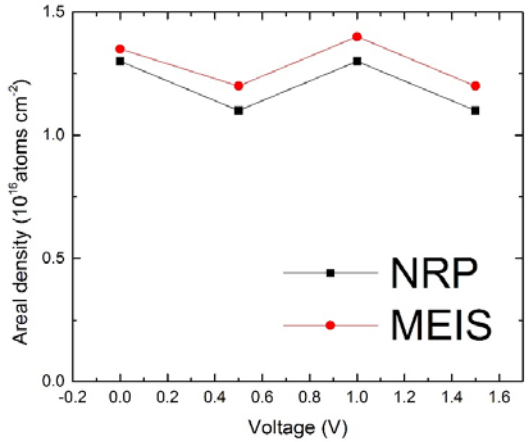
[1] G. Battistig et al. Nuclear Instruments and Methods B 61 (1991), [2] I.Baumvol. Surface Science Reports 36 (1999)

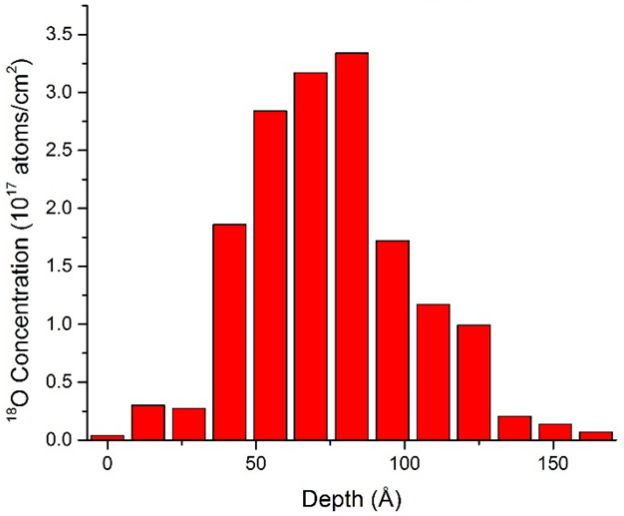
Nuclear Reaction Profiling ^{18}O (p, α) ^{15}N



Alpha intensity as a function of energy



Total areal density comparison of MEIS & NRP



1 V: 18O concentration as a function of depth

Two major oxide growth mechanism: Field assisted ion transport (FAIT) [1]

A

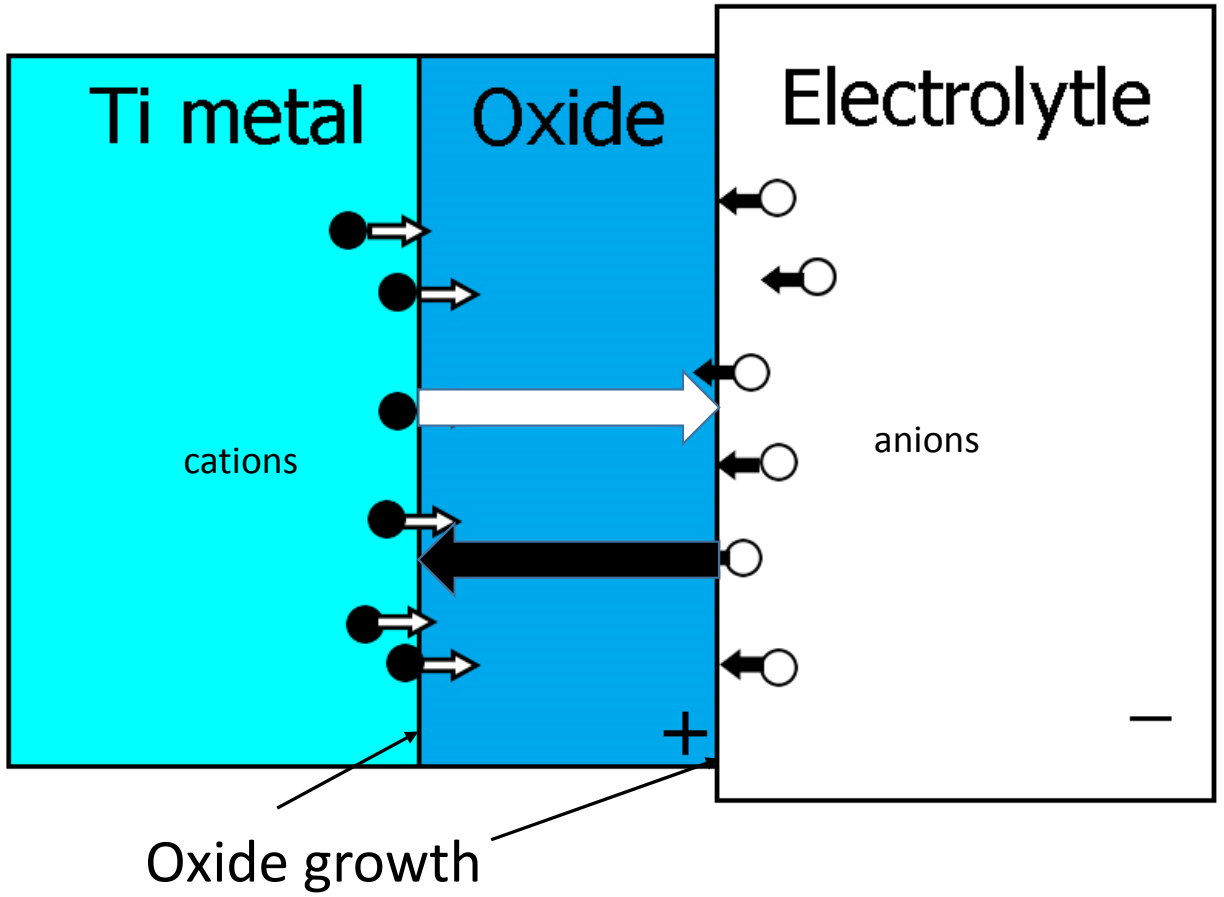
- Driven by electric field in oxide, about 4E8 V/m [2]
- Both cations and anions have mobility

t_O : fraction of oxide that grows due to Oxygen ions,

t_m: fraction of oxide that grows due to Metal ions

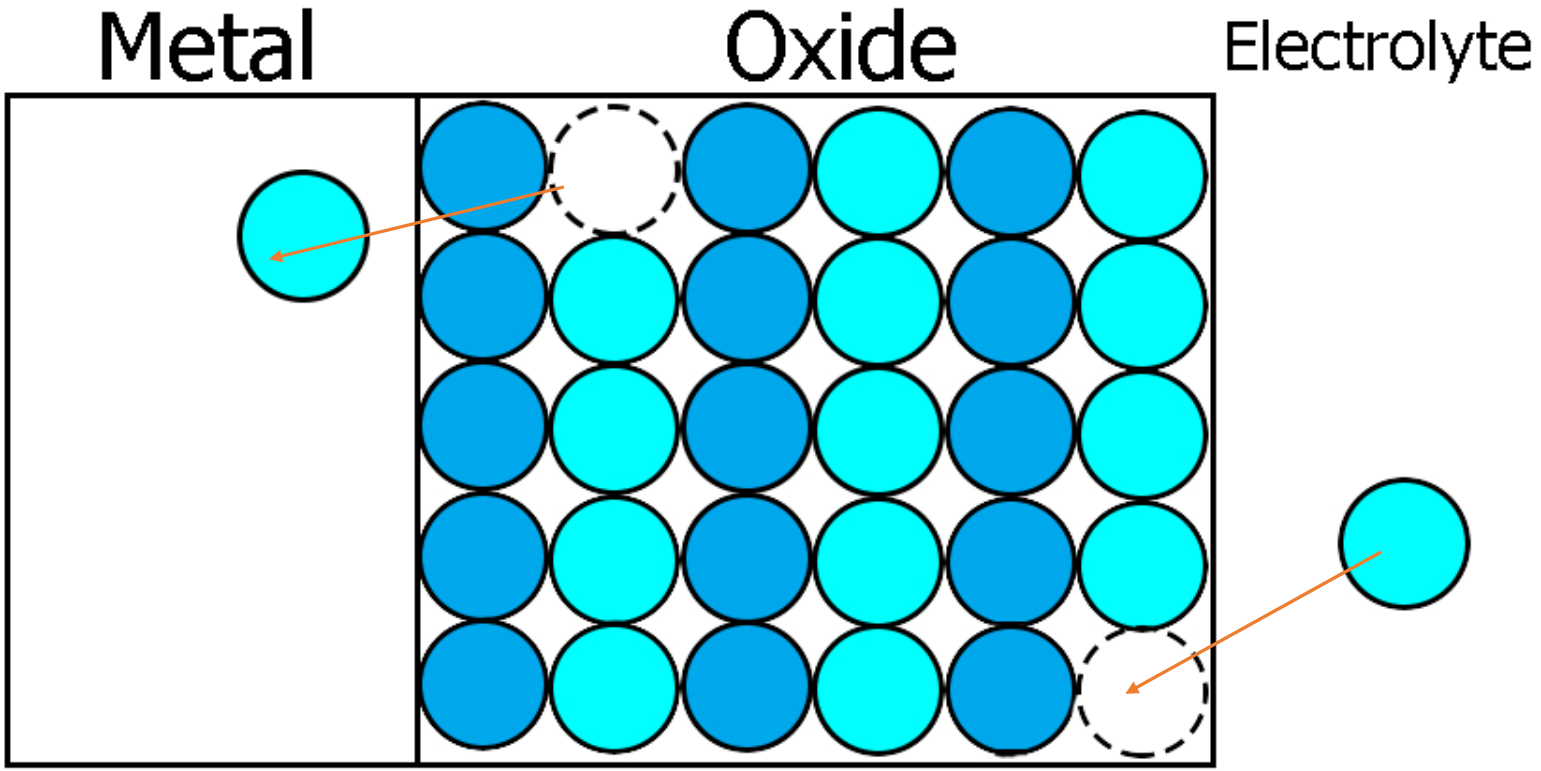
$t_m+t_O=1$

[3] Gives tm=0.35 and to=0.65



[1] L. Young, Anodic Oxide Films, Academic Press, London (1961). [2] Z. Tun et al., J. Electrochem. Soc. 146, 988 (1999), [3] N. Khalil and J.S.L. Leach, Electrochim. Acta 31, 1279–1285 (1986).

Two major oxide growth mechanism: Point-defect model (PDM) [3]

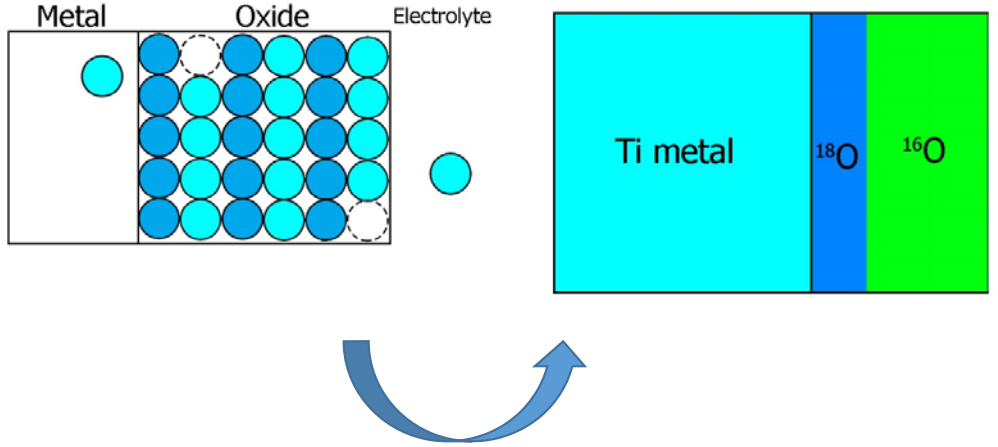


B

[3] D. D. Macdonald, J. Electrochem. Soc., 139, 3434 (1992).

Conclusions

- Oxide growth increases as function of voltage
- New oxide created by ^{18}O diffusing towards the oxide/metal interface



- Increasing incorporation of ^{16}O towards electrolyte/Oxide interface: O exchange

- Depth profiles consistent with the Point defect model
- In addition there is Ti diffusion [1]:

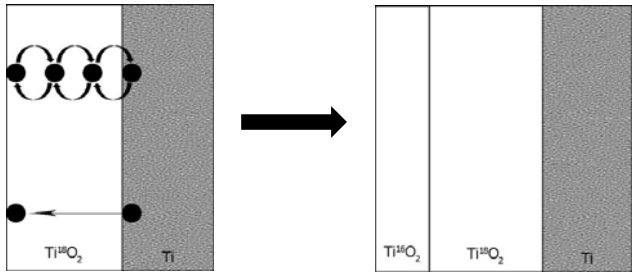
  -2.0x10^{-7} m^2/s for O in TiO_2

  -2.0x10^{-6} m^2/s for Ti in TiO_2

- proceeds by vacancy mechanism, separately on the O and Ti sublattices due to strong ionic chemical bond between constituents

Ti can be a mobile species

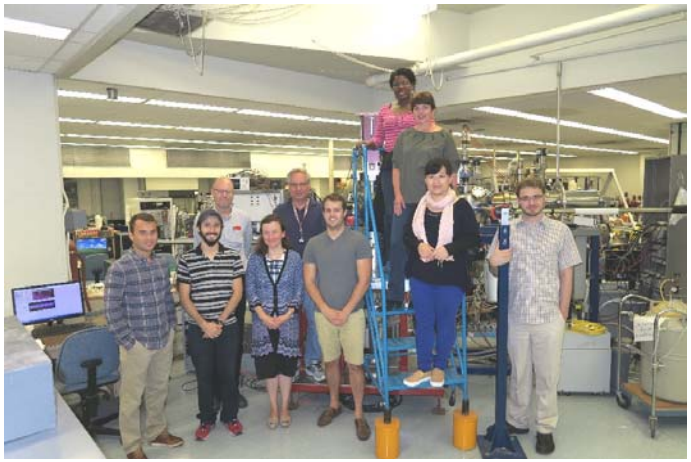
H_2O



Thank you!

I want to thank

- Lyudmila Goncharova, my supervisor
- My research group and fellow grad students
- Dr. J. Noel, Chemistry, UWO
- Jack Hendriks for Tandetron operation



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