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WP 5: Containment and sealing approaches for photovoltaic integrated water electrolysis

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Workpackage objectives and main tasks

Objective: to increase the lifetime of integrated PV-EC devices to ensure efficient operation with < 10% degradation over 6 months

Task description	
T 5.1	Define test structures, experimental set-up and protocol for rapid testing
T 5.2	Monolithic sealing layers
T 5.3	Non-monolithic sealing layers

Explanation of the concept

1. Sealing and packaging serve two main purposes:
   - To prevent leakage of electrolyte and product gases out of the device
   - To prevent ingress of external gas into the device

2. Proper choice of sealing and packaging materials has implications on
   - **Fire safety:** escape of hydrogen and/or oxygen resulting in formation of explosive gas mixtures
   - **Revenue loss:** via escape of generated hydrogen or its contamination via ingress of gas from the ambient
   - **Environmental pollution:** by spillage of corrosive electrolytes or water that has been in contact with heavy metals

3. Monolithic thin films are specifically used to protect the photoabsorber from corrosive electrolyte in photoelectrochemical (PEC) devices but have limited mechanical stability

4. Non-monolithic sealants e.g. gaskets, adhesives are used to prevent leakage into and out of PEC, integrated PV-EC and stand alone EC systems

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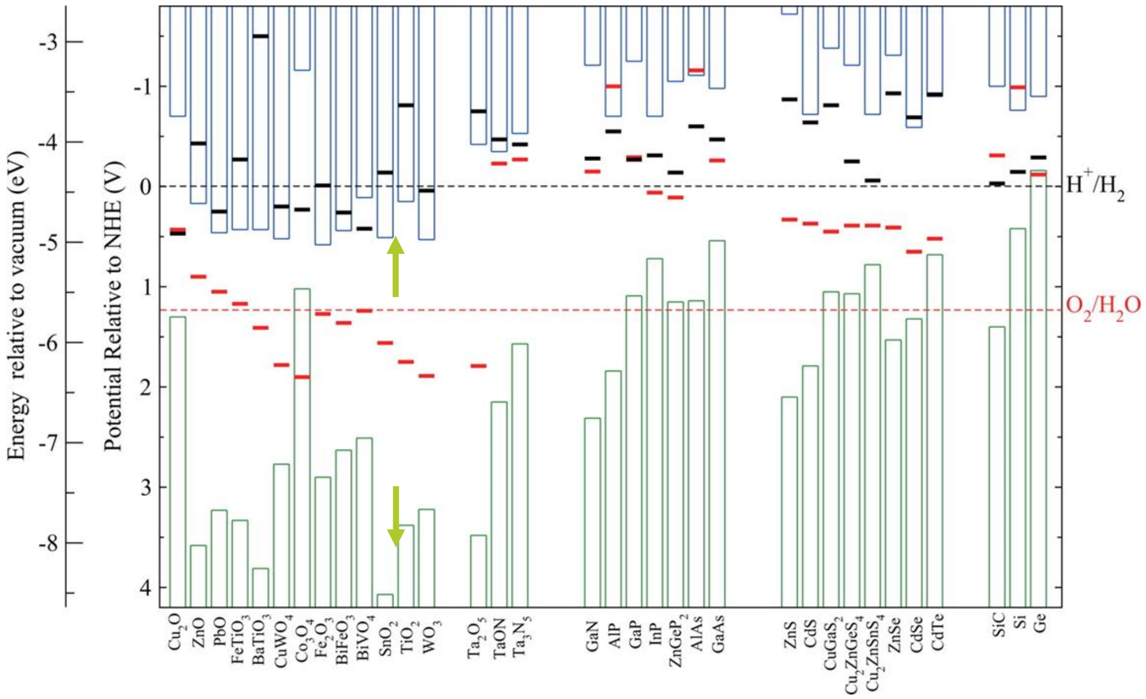
Main Results: Monolithic sealing layers

SnO_2 and TiO_2 are thermodynamically stable with respect to the water splitting process



– Reduction potentials
– Oxidation potentials

- pH = 0, 298.15 K
- 1 bar

Chen, et al. (**2012**) *Chem. Mater.* 24: 3659

Protective oxides tested on magnetron sputtered molybdenum

- Atomic layer deposition for conformal coverage
- For SnO_x: TDMASn + water, 25 nm
- For TiO_x: TDMATi + water, 20 nm
- Deposition temperature below 150 °C

Test parameters

- Open circuit potential E_{OCP} transient for 55 minutes
- Potentiodynamic polarization vs E_{OCP}
  - 5 mV/s scan from cathodic to anodic
  - Asymmetric: with - 250 mV to +1000 mV
- Electrochemical impedance spectrometry
  - D.C voltage : E_{OCP} and A.C voltage : 10 mV
  - 0.1 Hz to 1M Hz
- XPS analysis of protective oxide surface

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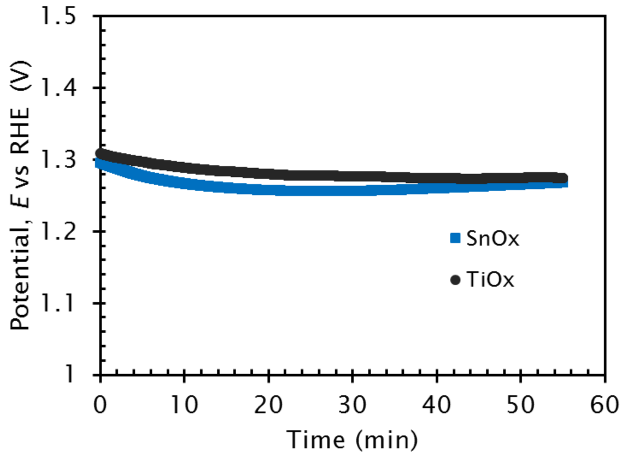
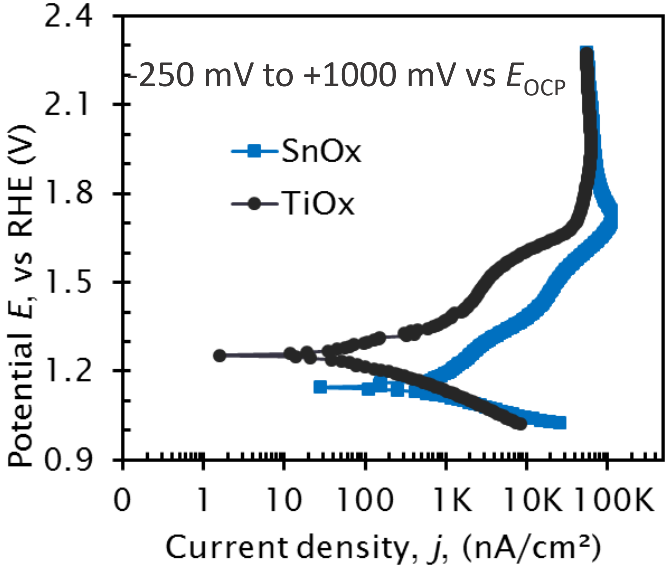
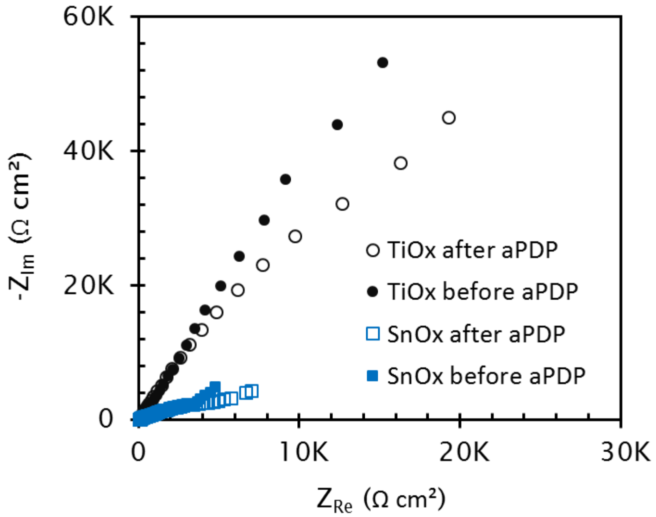
Main Results: Monolithic sealing layers

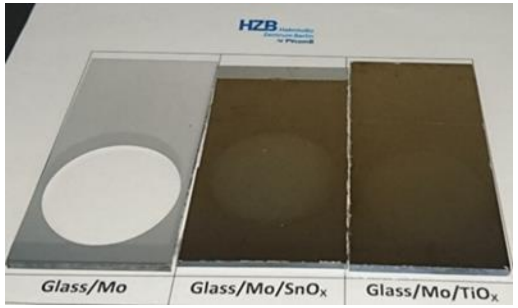


1.0 M KOH
Stagnant ~25°C





Open circuit potential E_{OCP} for more positive than redox potentials for H_2O/O_2 (+ 0.403 V vs. NHE) and H_2/H_2O (-0.826 V vs. NHE) at pH = 14 and 27°C.



$|Z|(f \to 0) \sim R_\Omega + R_{CT}$ (charge transfer resistance)
$|Z|, (f \to \infty) \sim R_\Omega$ (Uncompensated series resistance

Oxide	|Z| at 1.0 MHz		|Z| at 0.1 Hz (kΩ cm²)	
	Before	After	Before	After
TiO_x	47.3	47.8	55.3	48.9
SnO_x	57.6	57.1	6.8	8.2

TiO_x oxidised at a slower rate than SnO_x but probaby cannot provide extended protection beyond a few tens of hours

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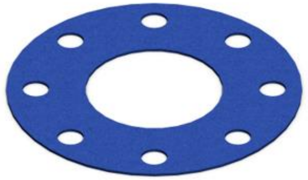
Main Results: Non monolithic sealing

Survey of non-monolithic sealings used for electrolysers and redox batteries by FZJ

O-rings



Flat gaskets

- Compressible o-rings or flat gaskets favoured
- Material chosen depends on the operating conditions
- **PEM electrolyser:** rubber, silicon plates with metal support frame, EPDM, PTFE and for (< 130 bar) carbon based gaskets
- **Alkaline electrolysers**: PTFE is favoured despite high cost
- **Redox flow batteries:** (highly acidic conditions at 0-40°C) ETFE, FEP, PTFE, FPM / FKM

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Main Results: Non monolithic sealing

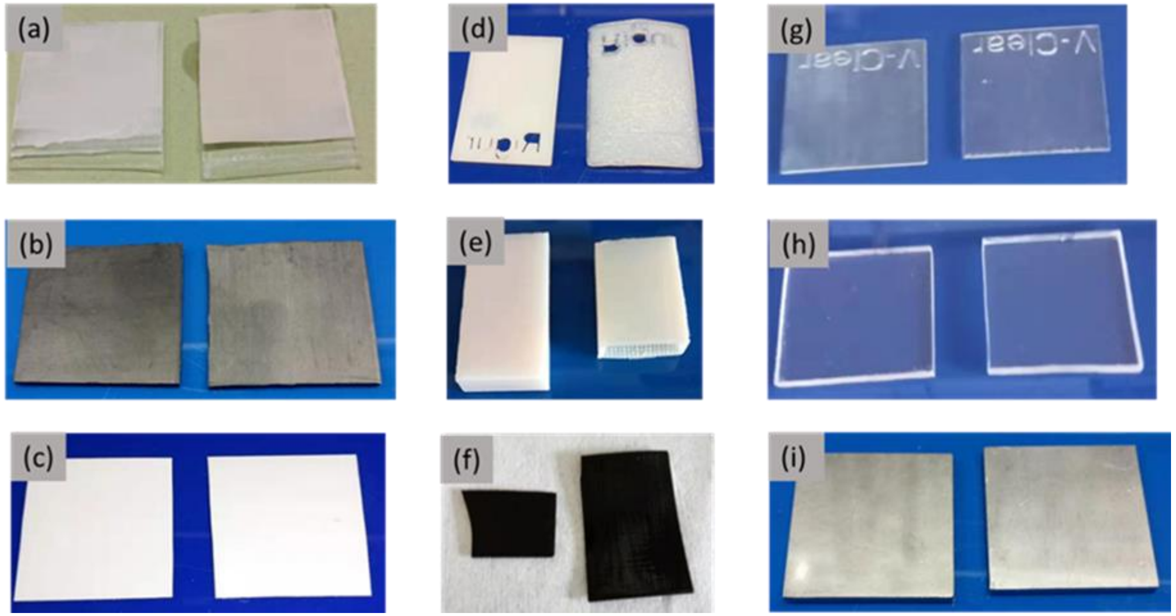
Survey of non-monolithic sealings used for photovoltaic modules

Material	Purpose
Ethylene vinyl Acetate (EVA)	Encapsulation
Poly vinyl butyral (PVB)	Encapsulation
Polyester	Back foil
Polyethylene terephtalate (PET) e.g dyMat	Back foil
Poly vinyl fluoride (PVF) e.g. Tedlar	Back foil
Polyvinylidene (PVDF) chemically inert	Back foil
Laminates e.g. PVF/PET/PVF; PVF/Al/PVF etc	Back foil
Polyisobutylene (PIB)	Edge sealing
Thermoplastic polyurethane (TPU)	Edge sealing
2 component silicones	Bonding and sealing junction boxes

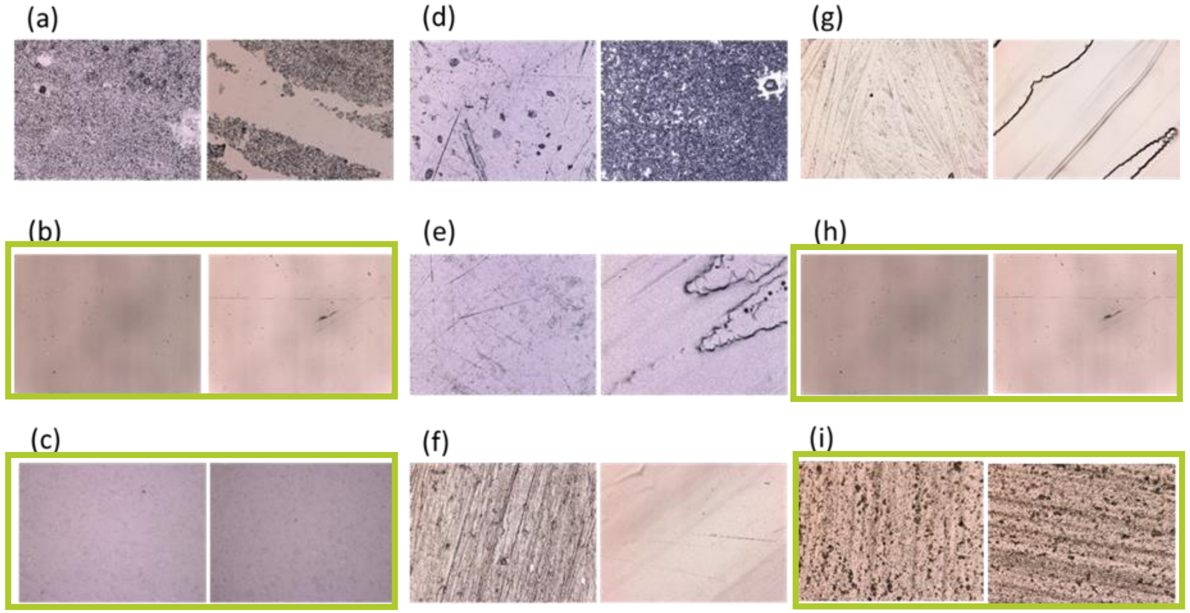
Sealing and encapsulating materials for PV modules are designed to withstand fluctuating temperatures, ultra-violet radiation exposure, salt and ammonia rich environments => possible synergies for PV-EC and PEC application

Main Results: Non monolithic sealing

- Identified sealing potential materials by reviewing state of the art in related devices
- Selection made based on availability
- Immersion test in 1.0 M KOH held at 60°C for 7 days



Laser microscope images corresponding to photographs

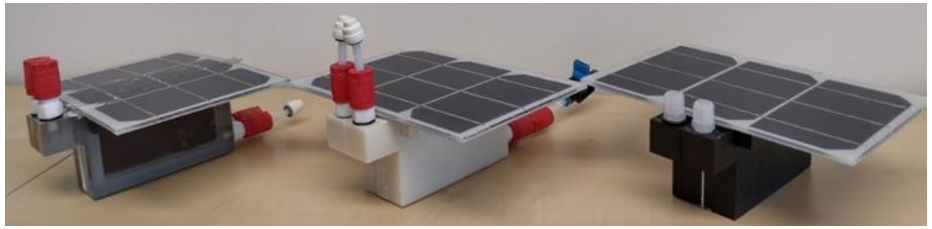


For each sample: left –before exposure and right – after exposure
a) LOCTITE® EA 9492 non-conductive adhesive on glass, (b) **EPDM**, (c) **Coveme Tedlar Dymat ®** PV backsheet, (d) 3D printed polypropylene based, Rigur, (e) Objet RGD525 HT, (f) VeroBlack, (g) 3-D printed PMMA derivative (VeroClear), (h) **bulk PMMA** (i) **316L stainless steel**. All 3D printed polymers are manufactured by Stratasys. Green indicates satisfactory performance

Main Results: Non monolithic sealing

Case study: Final sealant materials selected and implemented in a SHJ PV integrated electrolyser

Sealant Material		Purpose
LOCTITE® EA 9492 (Epoxy, 2:1)	(i) (ii) (iii)	Attaching the electrolysis cell frame onto the PV module Prevent leakage of electrolyte and product gas along the joint between the PV module and the electrolyser casing Avoid leakage of electrolyte and product gas along the edges of the electrolyser casing
EPDM gasket	(i)	Provide additional sealing at the joint between the anode and cathode compartment of the electrolyser spacing
Aremco-Bond 614 (Nickel containing epoxy)	(i)	Avoid contact between alkaline electrolyte and the electrical contacts between the PV module and the electrolyser cell
Veroclear-polymer (Stratasys)	(i)	Contain the electrolyte and product gases
Glass/ 0.6 mm EVA /PV cells/Polyethylene/ 0.3 mm Tedlar-PET-Tedlar	(i)	Protecting the PV module from moisture ingress and chemical corrosion. Laminates combine benefits of individual layers



VeroClear Objekt RGD525 HT VeroBlack

- PV integrated electrolyser using 3-D printed polymer Veroclear was operational for over 100 hours in outdoor conditions
- Leakage problems mainly at the junction between the electrolyser body and the tubing of the electrolyte
- Better solutions for sealing might exist but the cost is unacceptable if we want to hit the LCOH targets

Low weight, low cost materials favoured because load has to be partly borne by the "window" glass

Progress beyond state of the art and impact

- First detailed survey of different materials for containment and sealing of integrated PV materials published in the literature

- Lessons are adaptable to photoelectrochemical and photocatalytic devices

Publications and conference presentations

Peer reviewed publication

- S. Calnan, S. Aschbrenner, F. Bao, E. Kemppainen, I. Dorbandt and R. Schlatmann. *Prospects for Hermetic Sealing of Scaled-Up Photoelectrochemical Hydrogen Generators for Reliable and Risk Free Operation*. Energies 2019, 12(21), 4176.

Oral presentation at conference

- S. Calnan, F. Bao, S. Stickel, E. Kemppainen, R. Schlatmann. *Comparison corrosion-protection by titanium- and tin-oxide thin films for integrated photovoltaic-based water electrolyzers*. Electrochemistry 2018, 28 Sept 2018, Ulm, Germany.

Conclusions and Outlook

1. **Monolithic sealing layers still do not achieve** the required protection for long term stability of photoabsorbers in contact with electrolyte

2. Integrated PV-EC devices are now designed **to minimise or completely avoid electrolyte contact** with the photoabsorber => beneficial synergies with stand-alone PV modules and electrolyser technologies

3. Successful packaging and sealing of integrated PV-EC (and PEC) devices is challenging because one of the joints is always glass which is brittle and depends on
   - Expected operating conditions e.g. gas pressure, device temperature, fluctuations in weather conditions
   - Matching thermal coefficient of expansion of involved materials
   - Mechanical stength of the device components

4. Most reliable test for packaging and sealing materials is when incorporated in the integrated PV-EC and subjected to the typical operating conditions

5. Safety regulations shall play a role in the material choices for packaging and sealing

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Thank you for your attention!

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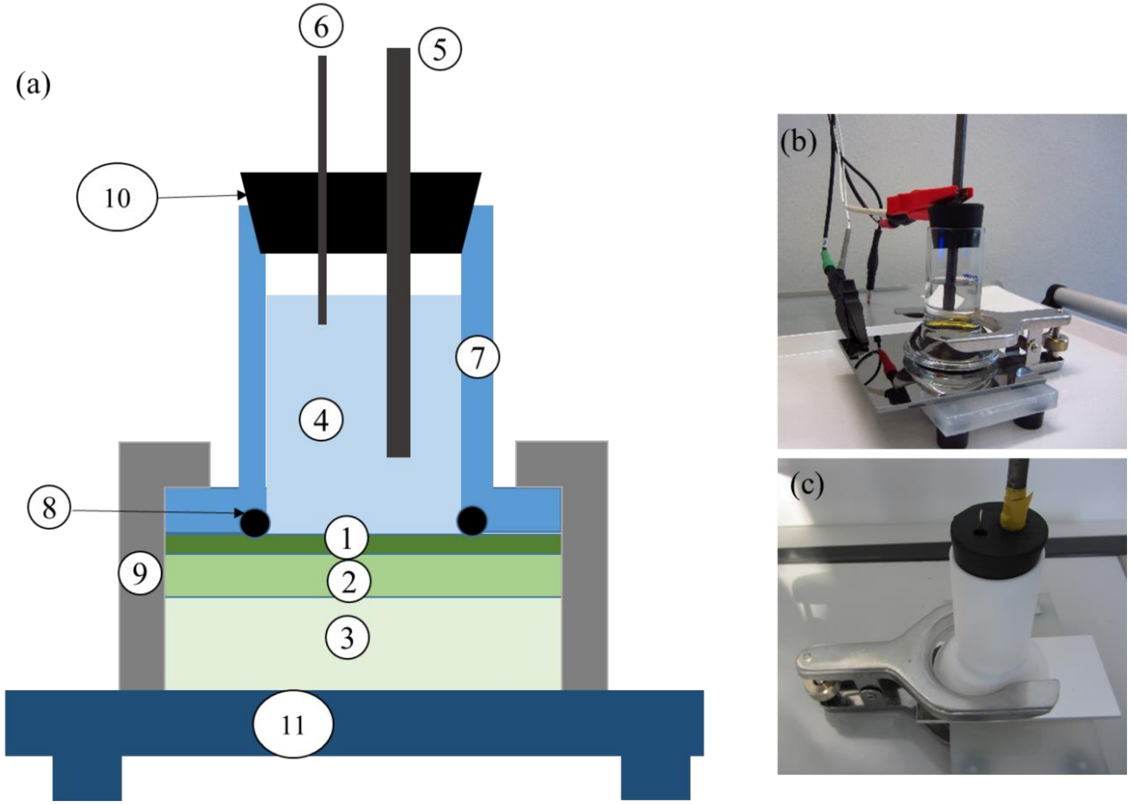
Electrochemical corrosion test set-up



(a) schematic of test set-up showing 1- monolithic sealant which acts as a working electrode in electrochemical tests; 2- thin film to be protected from corrosion; 3- supporting substrate for thin film; 4- electrolyte; 5-graphite counter electrode; 6- platinum wire as pseudo reference electrode; 7- glass or PTFE cell for containing electrolyte; 8-viton o-ring seal to prevent escape of electrolyte; 9- clamp for fixing o-ring; 10- rubber bung and 11- polymeric base to support clamping of the sample under qualification. Photographs (b) of the actual test set-up using a glass cell and (c) showing the PTFE cell which is more suited for studies with KOH.

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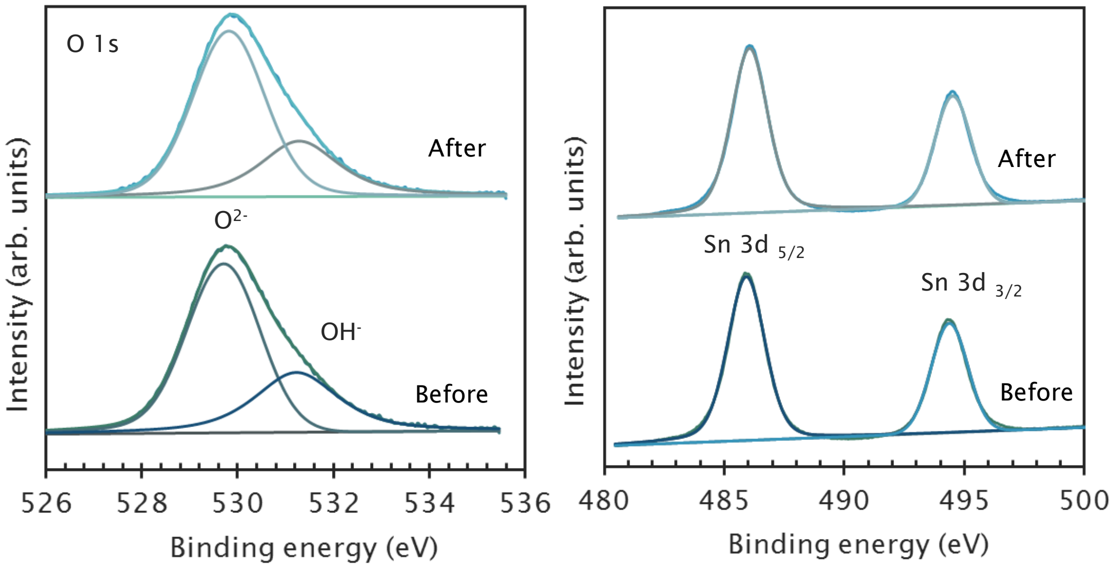
Surface chemistry for SnO_x



-250 mV to +250 mV vs E_{OCP}

Component	Before	After
	Percentage composition	
C	29.0	35.7
O	54.9	49.1
Sn	16.2	15.2
	Ratio	
[O]/[Sn]	3.4	3.2

Component	Specie	B. E (eV)	Before	After
% of O 1s	O^{2-}	529.8	67.6	69.0
	OH^-	531.2	32.3	31.0
% of C 1s	C-C	284.5	100	63.7
	C-O-C	286.6	0	15.1
	Shake-up	292.5	0	6.0
	Shake-up	296.2	0	15.2

Slight increase in SnO suggesting dissolution of the film indicating passive corrosion protection

* Only Sn^{3+} and not Sn^{4+} was detected

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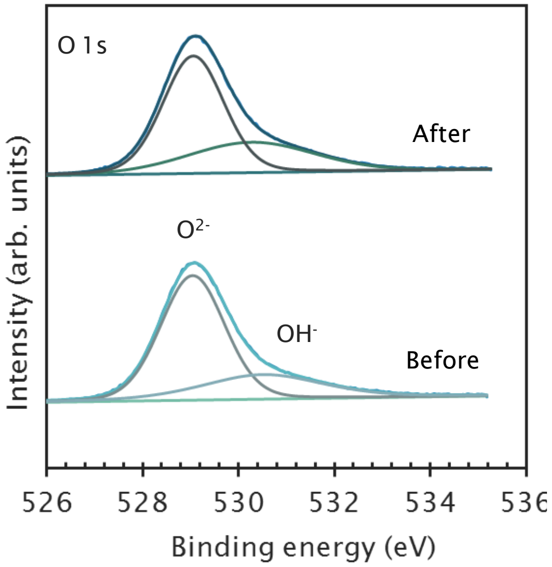
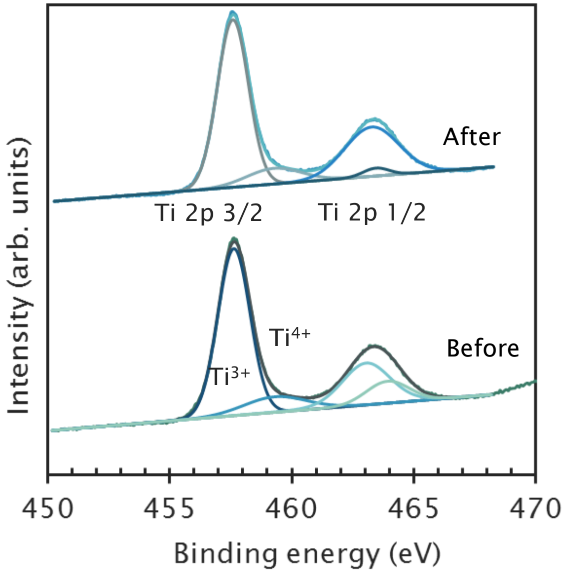
Surface chemistry for TiO_x





-250 mV to +250 mV vs E_{OCP}

Component	Before	After
	Percentage composition	
C	44.2	36.3
O	41.3	47.3
Ti	14.6	16.4
	Ratio	
[O]/[Ti]	2.8	2.9

Component	Specie	B. E (eV)	Before	After
% of Ti 2p 3/2	Ti^{4+}	459.3	15.2	14.1
	Ti^{3+}	457.6	84.8	85.9
% of O 1s	O^{2-}	529.1	71.0	65.9
	OH^-	530.3	29.0	34.1
% of C 1s	C-C	284.5	68.2	72.5
	C-O-C	286.0	33.7	22.4
	satellite	274.5	5.1	5.1

Increase in intermediate corrosion products e.g. $Ti(OH)_3$ suggests active protection

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