

Modeling Dye Sensitized Solar Cells Based on Nano-Tubes or Nano-Rods - A New Transmission Line Approach

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Outline

- A short reminder on the DSSC principle.
- Traditional treatment of frequency spectra from DSSC in literature: modeling is based on continuum theory.
- The alternative: consideration of the DSSC porous structure - the approach from K. West and L. Bay.
- The homogeneous pores model by H. Göhr and its recent photo-electrochemical expansion.
- Experimental: EIS-, CIMPS & CIMVS characterization of thin film DSSC based on TiO_2 -nanotube electrodes.
- The application of the new model to the experimental results.

The DSSC Basics

- In Dye Sensitized Solar Cells, DSSC, the electrons generated by photon absorption inside the dye molecules appear at the surface of the semi-conducting oxide material and mostly not in direct vicinity to the current collecting photo-anode.
- The efficiency of a DSSC suffers from the competition between charge transport- and loss processes of the photoelectrons on the way from the site of generation to the electrical contact.

L. Bay, K. West / Solar Energy Materials & Solar Cells 87 (2005) 613–628

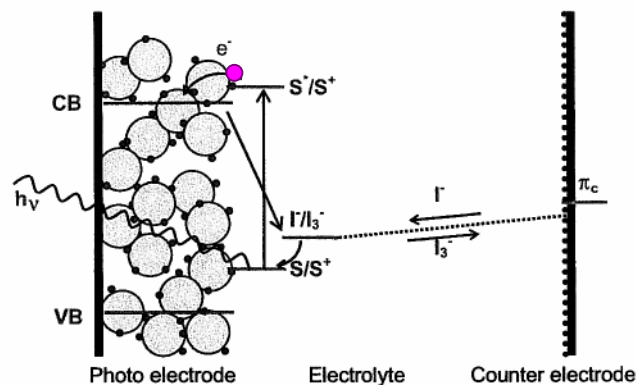
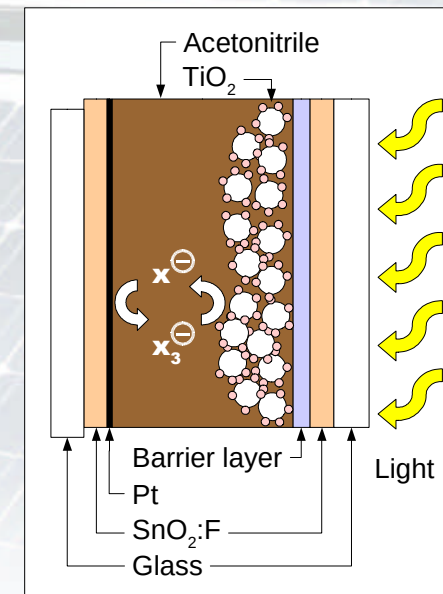
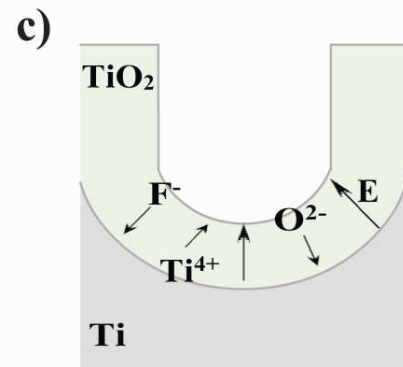
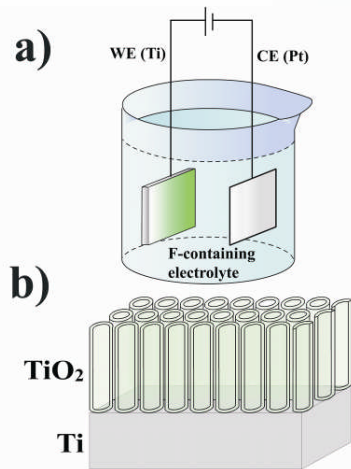


Fig. 1. Sketch of the geometry and energy levels in a DSSC.

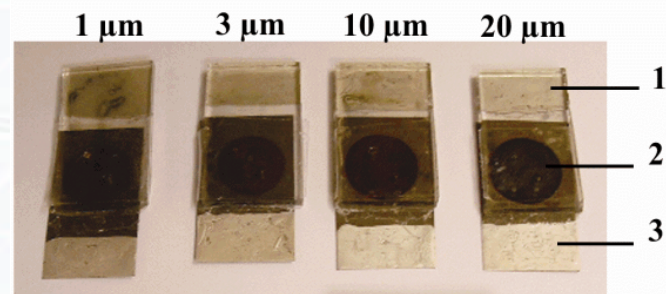


Highly Ordered Oxides - The Solution?



- a) Schematic of the high-E-field (voltage $\approx 100V$) anodization procedure. Electrolyte was based on ethylene glycol, containing 0.5M HF [1].
- b) Sketch of the TiO₂ nano-tube layer on Ti.
- c) Scheme of the self organizing process controlled by the competition of anodic formation and F⁻-induced etching of TiO₂ [2].

Photograph of the thin film DSSC based on TiO₂-nano-tubes built for testing.



- 1 cathode: FTO covered with Pt
- 2 dye loaded TiO₂ nano-tubes of different length in I⁻/I₃⁻ containing electrolyte.
- 3 Ti-foil as oxide carrier and anode

[1] R. Beranek, H. Hildebrand, P. Schmuki, *Self-organized porous titanium oxide prepared in H₂SO₄ / HF electrolytes*, Electrochem. Sol. State Lett. 6 (3), B12 (2003).

[2] A. Ghicov, P. Schmuki, *Self-ordering electrochemistry: a review on growth and functionality of TiO₂ nanotubes and other self-aligned MOx structures*, Chem. Commun. 20 (2009) 2791.

The Traditional Modeling Approach

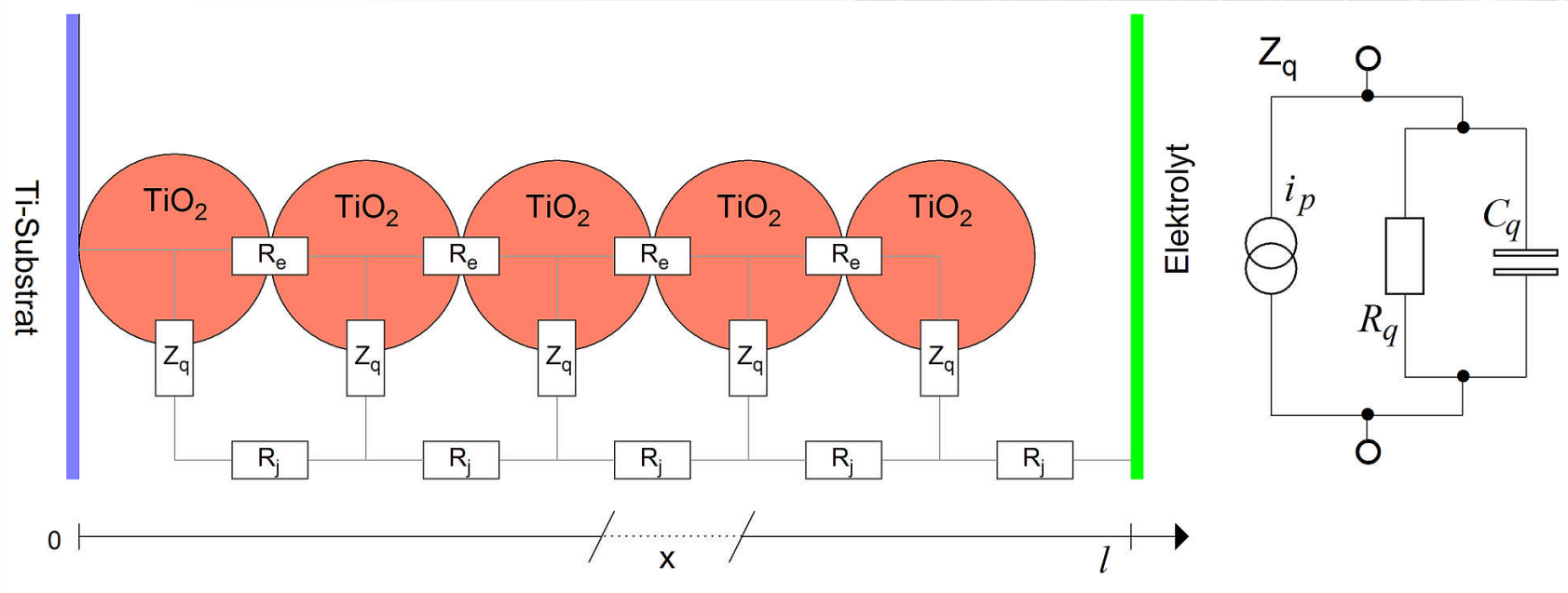
- Intensity Modulated Photo Spectroscopy of current, IMPS, and voltage, IMVS, are popular techniques for the investigation of the DSSC dynamic efficiency. They are usually interpreted in terms of electron diffusion- and recombination time constants (see for instance [3]).
- For the theoretical derivation, generation, transport and recombination are put together in form of a continuity equation. The differential equations are solved according to the actual boundary conditions (see for instance equ. 1-3 [4]).
- The porous distributed nature of such systems is not considered explicitly. Instead, „effective“ (due to electron “trapping”) diffusion coefficients are used.

[3] J. Bisquert, V.S. Vikhrenko, *Interpretations of the Time Constants Measured by Kinetic Techniques in Nanostructured Semiconductor Electrodes and Dye-Sensitized Solar Cells*, J. Phys. Chem. B 108 (2004) 2313-2322.

[4] J. Krüger, R. Plass, M. Grätzel, P. J. Cameron, L. M. Peter, *Charge Transport and Back Reaction in Solid-State Dye-Sensitized Solar Cells: A Study Using Intensity-Modulated Photovoltage and Photocurrent Spectroscopy*, J. Phys. Chem. B 107 (2003) 7536-7539.

Porous Photo Electrode Models

- L. Bay & K. West [5] developed a model which takes into account the distribution of photocurrent generation and loss along the chain ladder, built from the porous network of oxide and electrolyte.



[5] L. Bay, K. West, *An equivalent circuit approach to the modeling of the dynamics of dye sensitized solar cells*, Solar Energy materials and Solar Cells, 87 (2005) 613.

Porous Photo Electrode Model by Bay & West

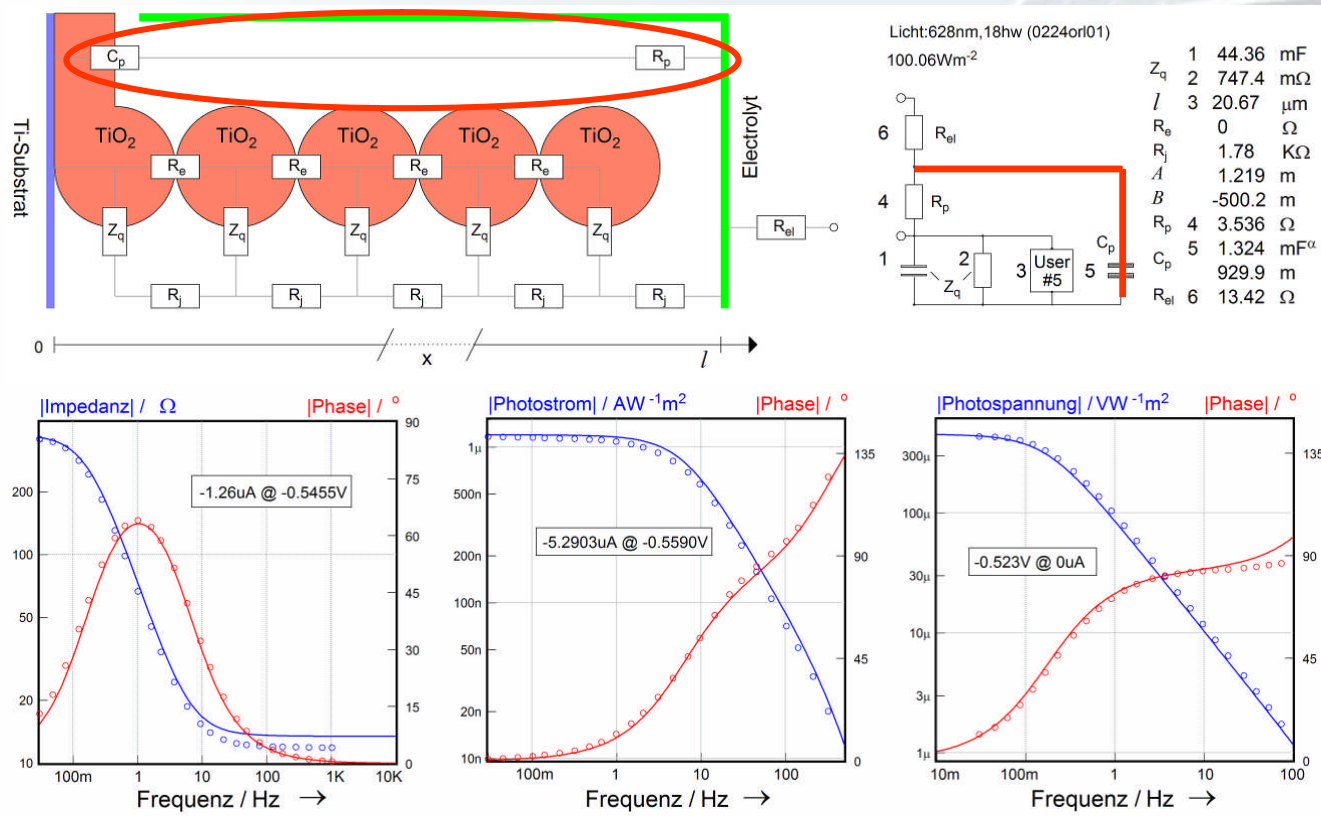
- Expression for the dynamic photo voltage U_γ found by Bay & West [5]

$$U_\gamma = \frac{B \cdot A \cdot R_i}{A^2 - \alpha^2} \left[e^{-A \cdot l} \left(1 + \frac{A}{\alpha} \coth(\alpha \cdot l) \right) - \frac{A}{\alpha \sinh(\alpha \cdot l)} + \right. \\ \left. 1 - \frac{A}{\alpha} \coth(\alpha \cdot l) + \frac{A}{\alpha \sinh(\alpha \cdot l)} \cdot e^{-A \cdot l} \right] \quad \text{after [5], Equ. 9}$$

(R_e , R_i : electronic and ionic resistance [$\Omega \cdot \text{cm}$], B : quantum efficiency, A : absorption coefficient [cm^{-1}], l : porous system depth [cm], α : shortcut using $\alpha^2 = (R_e + R_i) / Z_q$, [α] = cm^{-1}) with the photo-electrochemical active surface impedance Z_q . In equivalence to the continuum model diffusion coefficient D_n and recombination time constant τ_n are found to $D_n = [C_q \cdot (R_i + R_e)]^{-1}$ $\tau_n = R_q \cdot C_q$.

[5] L. Bay, K. West, *An equivalent circuit approach to the modeling of the dynamics of dye sensitized solar cells*, Solar Energy materials and Solar Cells, 87 (2005) 613.

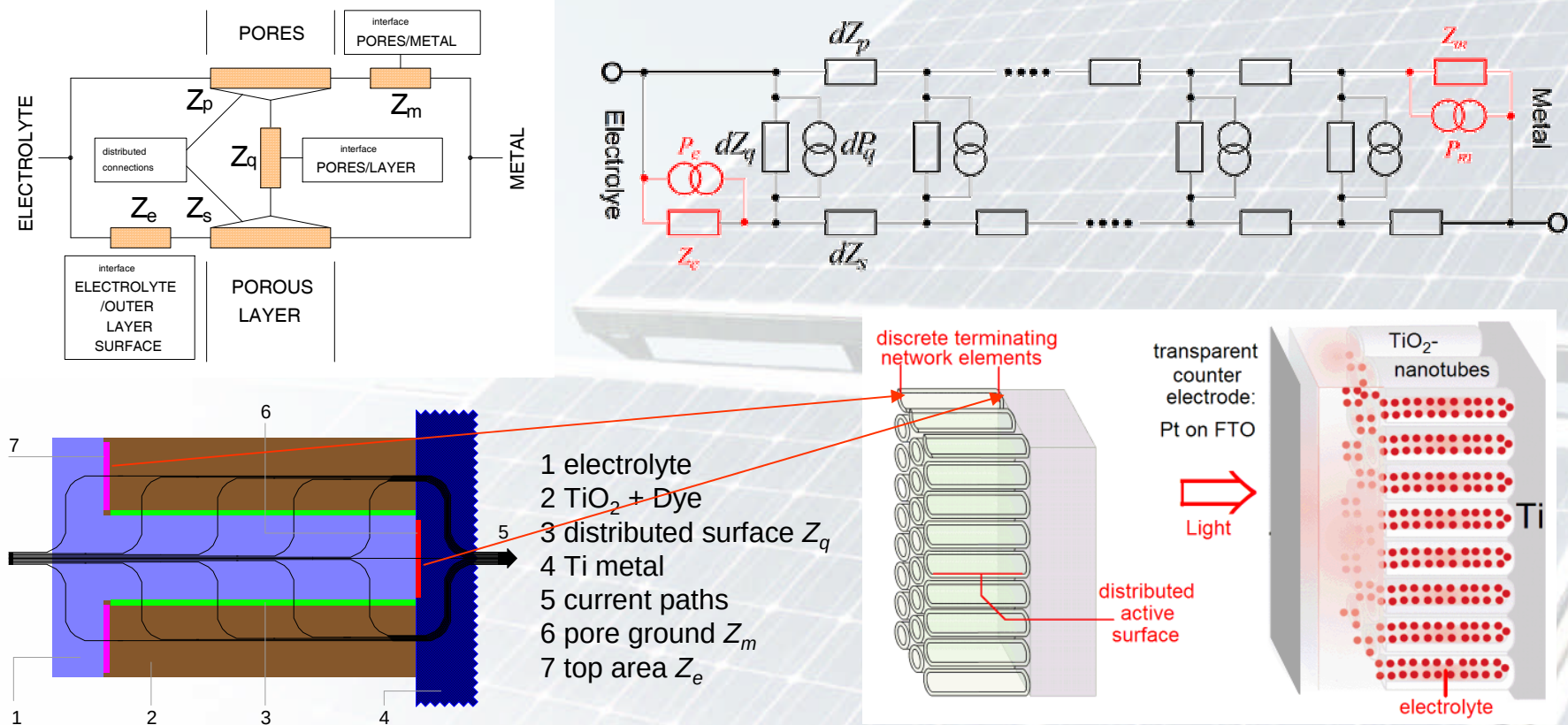
Application of the Bay & West Model on an Isolated Nanotube Photoanode



[6] C.-A. Schiller, *Optimierung der dynamischen Transferfunktionsanalyse für die Impedanzspektroskopie und die intensitätsmodulierte Photospektroskopie zur Anwendung an instationären und verteilten elektrochemischen Systemen*, Dissertation Erlangen, August 2012, cpt. 7.7.2.

Porous Photo Electrode Models

- Impedance model for a homogeneous pore system [7] and its recent photo-electrochemical expansion



[7] H. Göhr, *Impedance Modeling of Porous Electrodes*, Electrochemical Applications, ZAHNER-elektrik, 1, 7-9 (1997), www.zahner.de/downloads/ea1997.pdf.

The New Porous Photo Electrode Model

- Expression for the dynamic photo voltage U_γ derived by Böhmer [8]

$$U_\gamma = B \cdot Z_p \cdot \left\{ \left(C - \frac{Z_p + Z_s}{C^2 - v^2} e^{-Aa} - [1 - e^{-Aa}] \right) \cdot \left(v + \frac{Z_s}{Z_p} \left[v \cosh(v) + \frac{Z_p + Z_s}{Z_e} \sinh(v) \right] \right) \right. \\ \left. + \left(C - \frac{Z_p + Z_s}{C^2 - v^2} - [1 - e^{-Aa}] \right) \cdot e^{-C - Aa} \left(\frac{Z_s}{Z_p} v + \left[v \cosh(v) + \frac{Z_p + Z_s}{Z_m} \sinh(v) \right] \right) \right\} \\ / \left[\left(v^2 + \frac{(Z_p + Z_s)^2}{Z_e \cdot Z_m} \right) \sinh(v) + v \cdot (Z_p + Z_s) \cdot \left(\frac{1}{Z_e} + \frac{1}{Z_m} \right) \cosh(v) \right] \\ + \frac{C \cdot B \cdot Z_p}{C^2 - v^2} \left(e^{-C} + \frac{Z_s}{Z_p} \right) e^{-Aa}$$

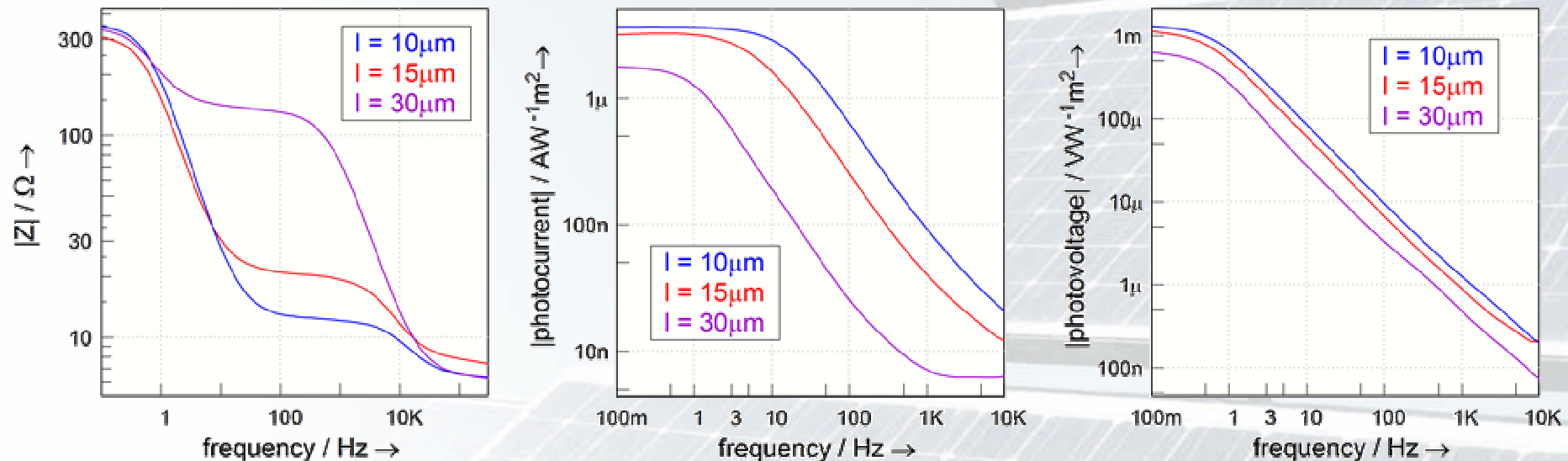
$v = d \cdot \sqrt{\frac{Z_p + Z_s}{Z_q}}$
 $C = A \cdot d$

Expression for the case of
oxide rear side illumination

Terminology according to H. Göhr, and with B = photocurrent equivalent to the total photon count/s, photon absorption C and layer thickness d of the porous system, photon absorption Aa and layer thickness a of pore ground or mouth

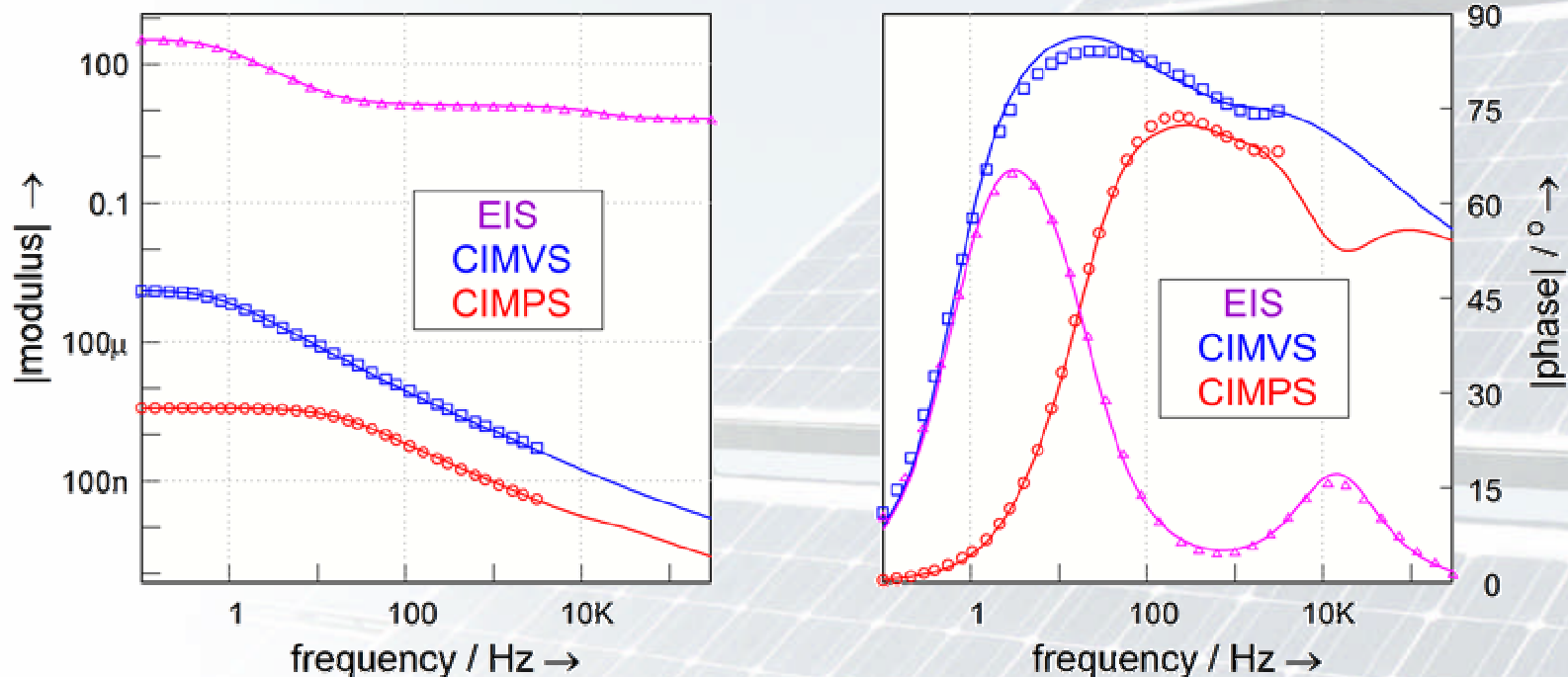
- [8] C. Böhmer, *Equivalent circuit model of the dye sensitized solar cell (DSSC) with top and bottom impedance*, unpublished.

Typical Results of the Dynamic Measurements



From left to right: EIS-, CIMPS- and CIMVS spectra (modulus) of thin film DSSC based on TiO_2 -nanotubes of different tube length l . Measurement was performed at the maximum power point bias under 400 W/m^2 white light illumination after hours of settling.

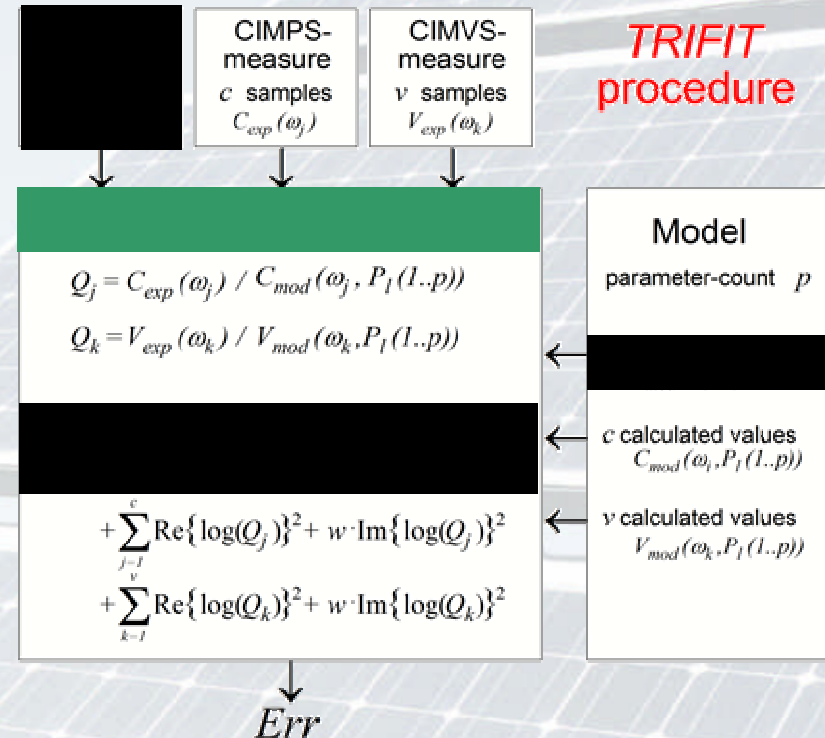
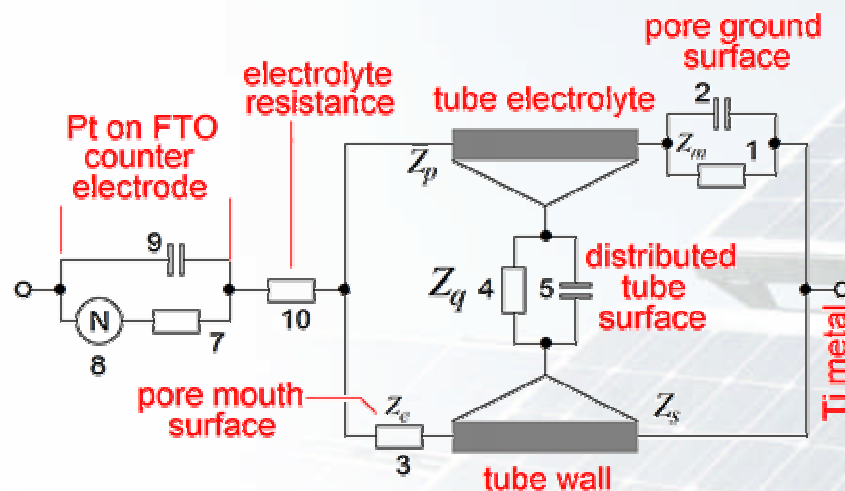
A Typical Fitting Result Using the Recent Model



Bode diagrams of a thin film DSSC built from $10\mu m$ TiO_2 -nanotubes. Measurement was performed at the maximum power point bias under $400 W/m^2$ white light illumination. Measurement samples are shown as symbols and the *TRIFIT* fitting results using the new model are drawn as solid lines.

Modeling & Fit

1	1.806	KΩ	6	4.441	μA	7	5.379	Ω
2	264.2	μF	Z_p	4.431	Ω	8	20.95	Ω·s ^{-1/2}
3	5.702	KΩ	Z_s	5.208	Ω		17.93	s ⁻¹
4	428.1	Ω	P_x^g	2.094		9	2.735	μF
5	494.7	μF	$P_{e,wy}^g$	62.08	m	10	4.303	Ω



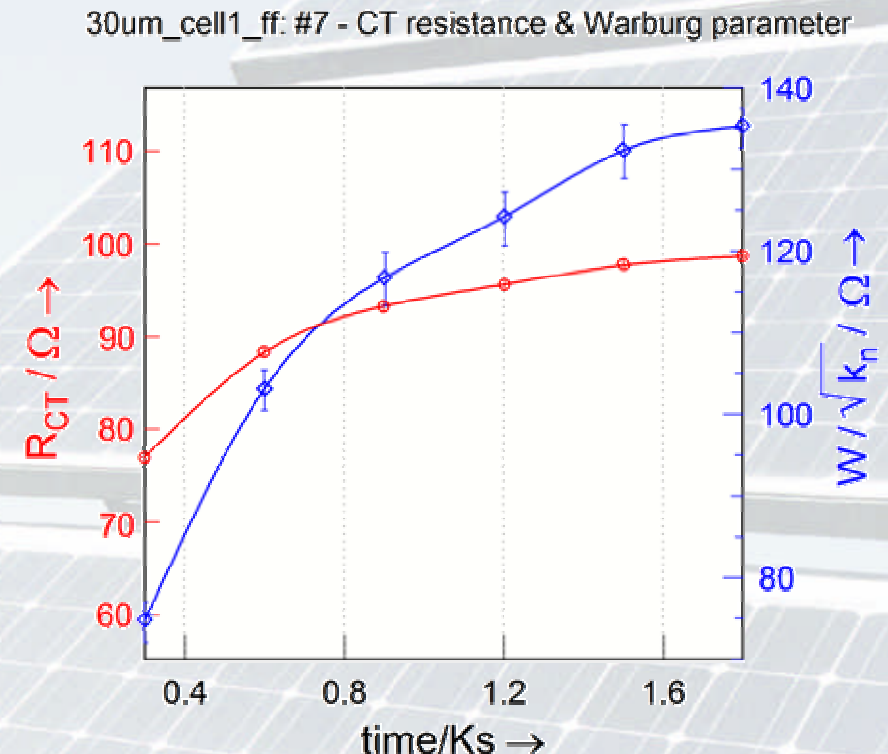
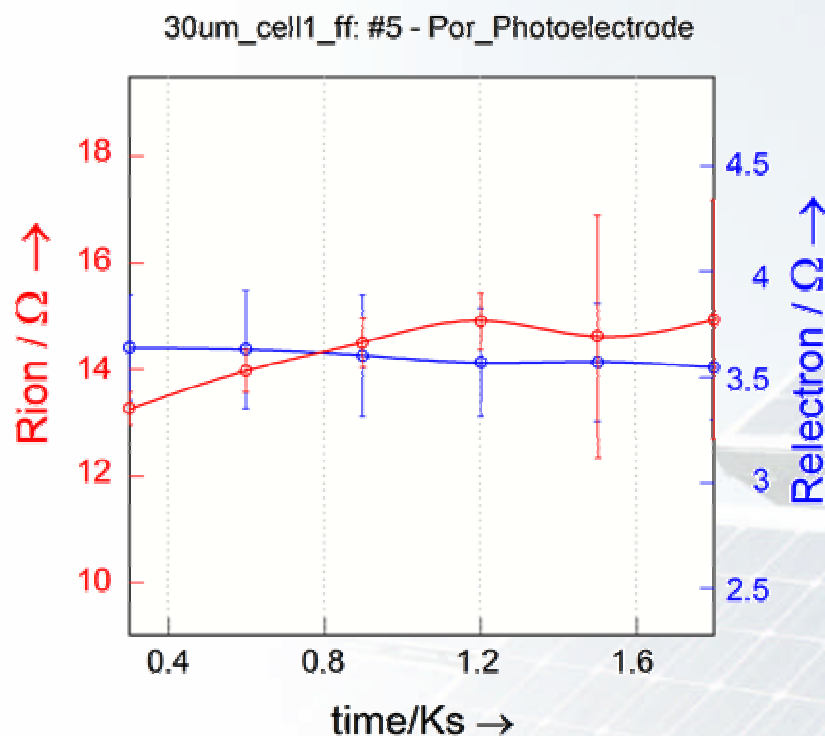
Left: Equivalent circuit used for the fit of the EIS, CIMPS and CIMVS spectra of a thin film DSSC built from 10μm TiO₂-nanotubes at OCP and at the maximum power point (400 W/m² white light). Right: Scheme of the *TRIFIT* fitting error calculation.



Discussion of the Results

- **Problem reproducibility:** Still individual preparation differences cause statistical data scatter of a magnitude comparable to the systematic dependency from the tube length.
- **Problem load dependency:** DC- and Dynamic measurements under load exhibit drift: the photocurrent decreases significantly with time. These changes are mostly reversible.
- The initial DC as well as the dynamic efficiency under load are best for the longest tubes.
- But the relative efficiency loss is also maximal for the longest tubes: in the stationary case after hours the efficiency sequence may be even inverted.
- A possible explanation could be, that the electrolyte in the pores builds up a concentration profile under load: the number of charged species decreases ($3\text{I}^- + 2\text{h}^+ \rightarrow \text{I}_3^-$) and the effective resistance of the electrolyte chain ladder stringer increases. But the results from the model fitting showed, that this effect is not sufficient to explain all of the drift:

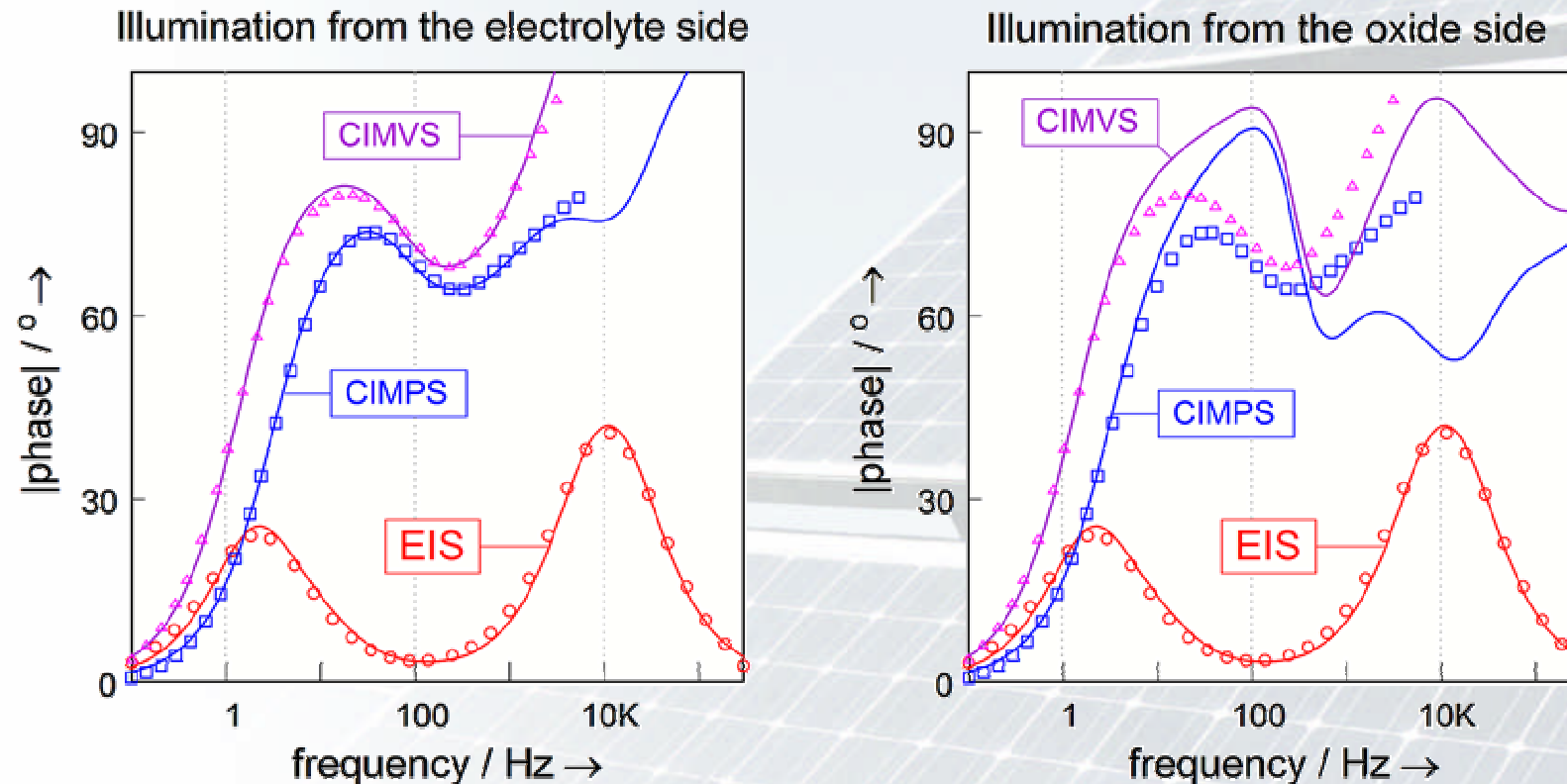
Drift of the Equivalent Circuit Parameters vs. Time



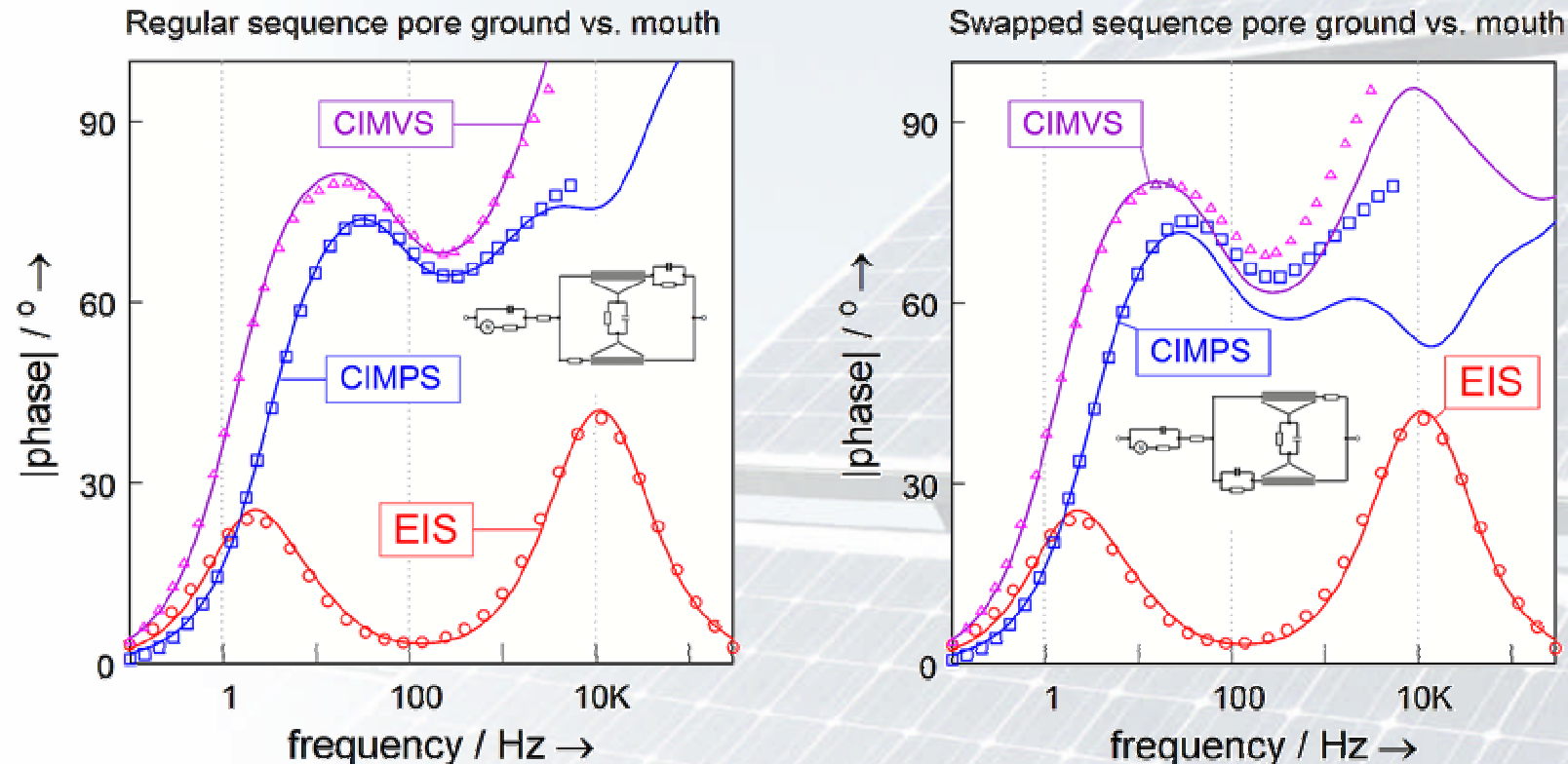
Left: time drift of the pores systems electronic [8] and ionic conductivity.
Right: time drift of the charge transfer resistance and of the Warburg impedance low frequency limit resistance of the counter electrode.

[9] A. Tighineanu et al. / Chemical Physics Letters 494 (2010) 260–263

Significance of the Model: Change of Illumination Direction



Significance of the Model: Assignment of Pore Ground- and Mouth Components





Conclusions

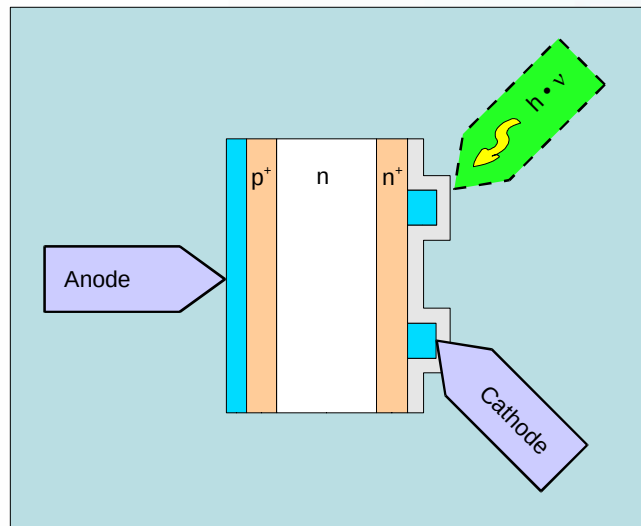
- The Pt on FTO counter electrode causes most of the efficiency decline with time of the TiO_2 nanotube based thin film DSSC.
- A new equivalent circuit approach allowed a clear assignment.
- The equivalent circuit model can be confirmed by the *TRIFIT* procedure fitting three different types of transfer functions, EIS-, CIMPS- and CIMVS, all from the same system state of the sample.
- Generally, a model, fitting EIS-, CIMPS- and CIMVS together avoids the ambiguity of isolated EIS measurements and is therefore definite with high probability.

Thank You for Your Attention!

The Principle of IMPS/IMVS: Light Intensity Modulation.

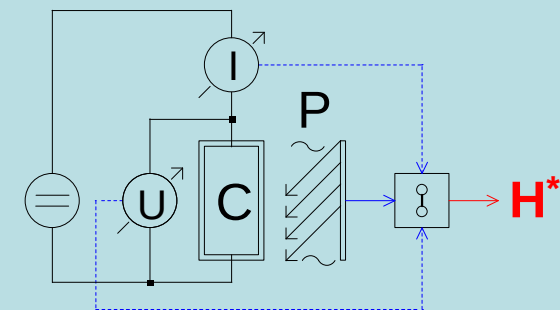
Besides EIS, two additional force-response couples can be used for further transfer function analysis:

- EIS: Dynamic voltage vs. current at constant intensity.
- IMPS: Dynamic photocurrent vs. intensity at constant voltage.
- IMVS: Dynamic photovoltage vs. intensity at constant current.



The point is:
Each transfer function emphasizes different parts of the system under test !

EIS / IMPS / IMVS

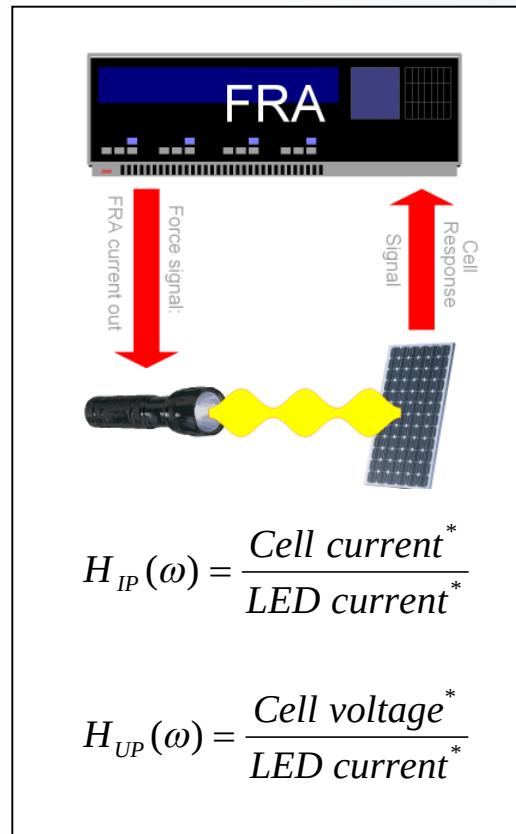


$$H_{UI}(\omega) = \frac{U^*}{I^*}, \quad [H_{UI}] = 1 \frac{V}{A} = 1 \Omega$$

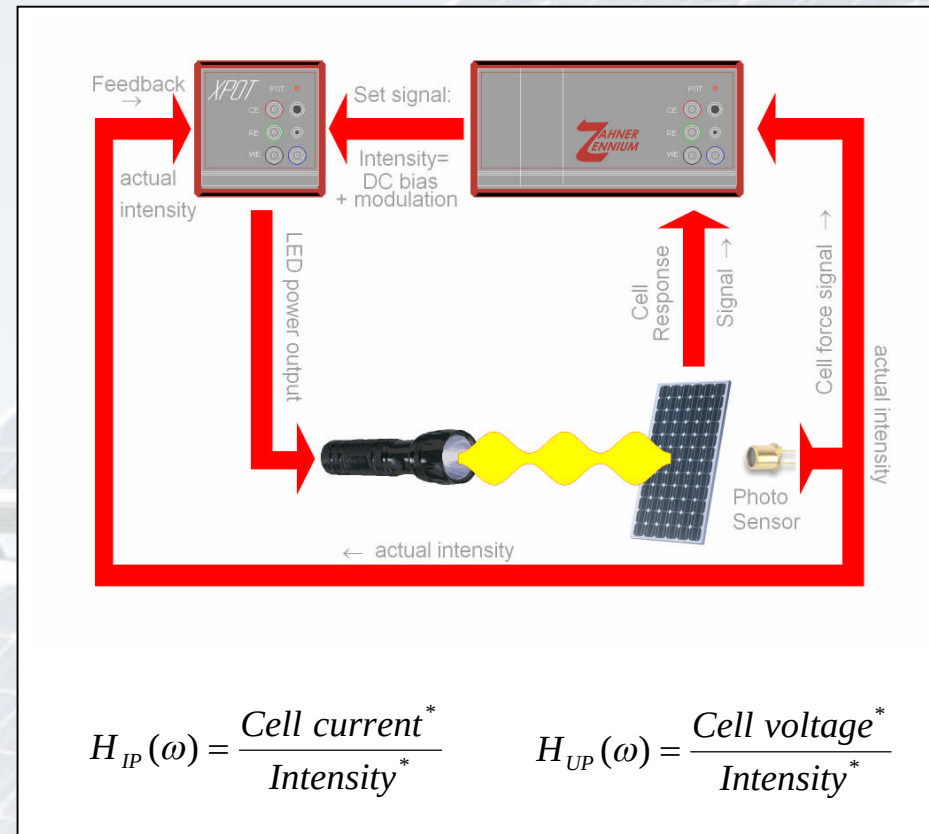
$$H_{IP}(\omega) = \frac{I^*}{P^*}, \quad [H_{IP}] = 1 \frac{A \cdot m^2}{W}$$

$$H_{UP}(\omega) = \frac{U^*}{P^*}, \quad [H_{UP}] = 1 \frac{V \cdot m^2}{W}$$

Comparison Between Conventional IMPS and CIMPS



Conventional IMPS: The LED control current is used as substitute for the intensity information. The actual intensity and modulation is uncertain.

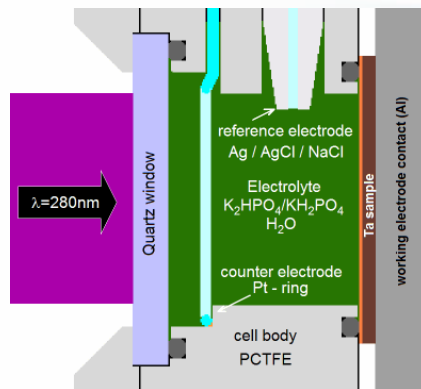
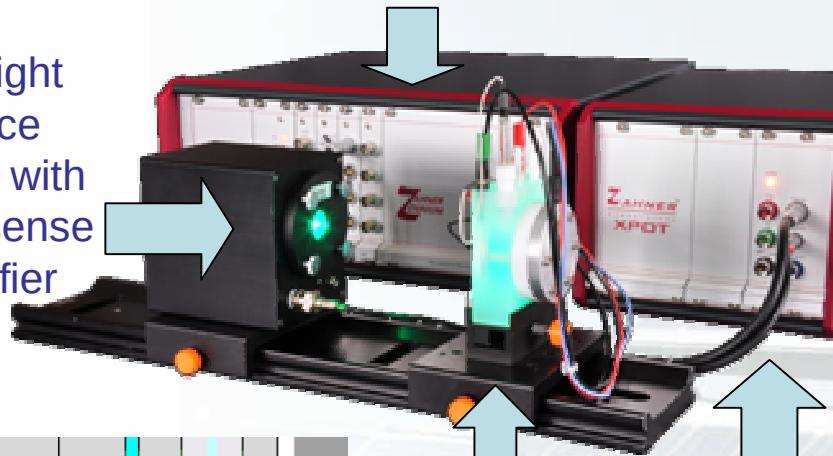


CIMPS: The measured intensity is used as force signal information. The actual intensity is controlled with a photo-sensor at the site of the cell and regulated by means of an operational amplifier feedback circuit.

Photo-Electrochemical Set Up

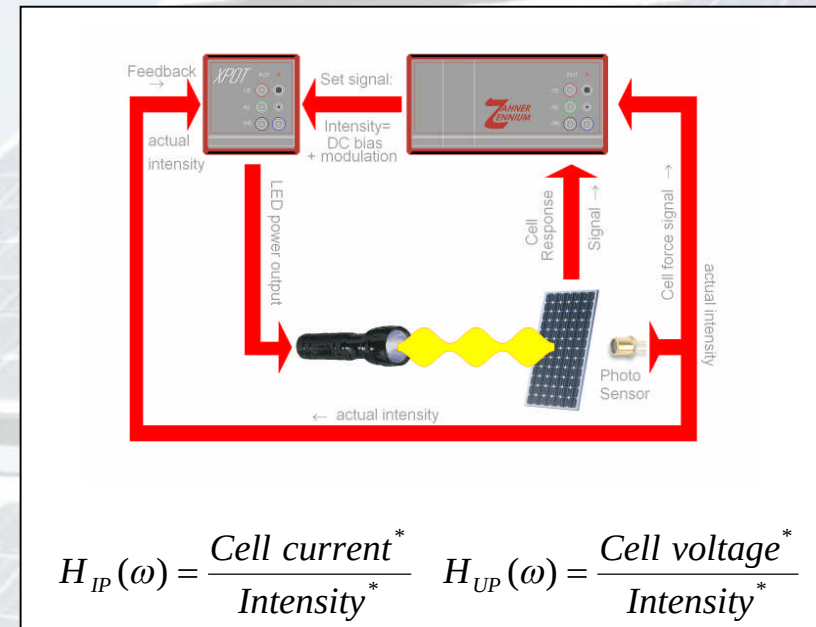
Zennium Electrochemical Workstation

LED light
source
280nm with
photo-sense
amplifier



PECC intersection

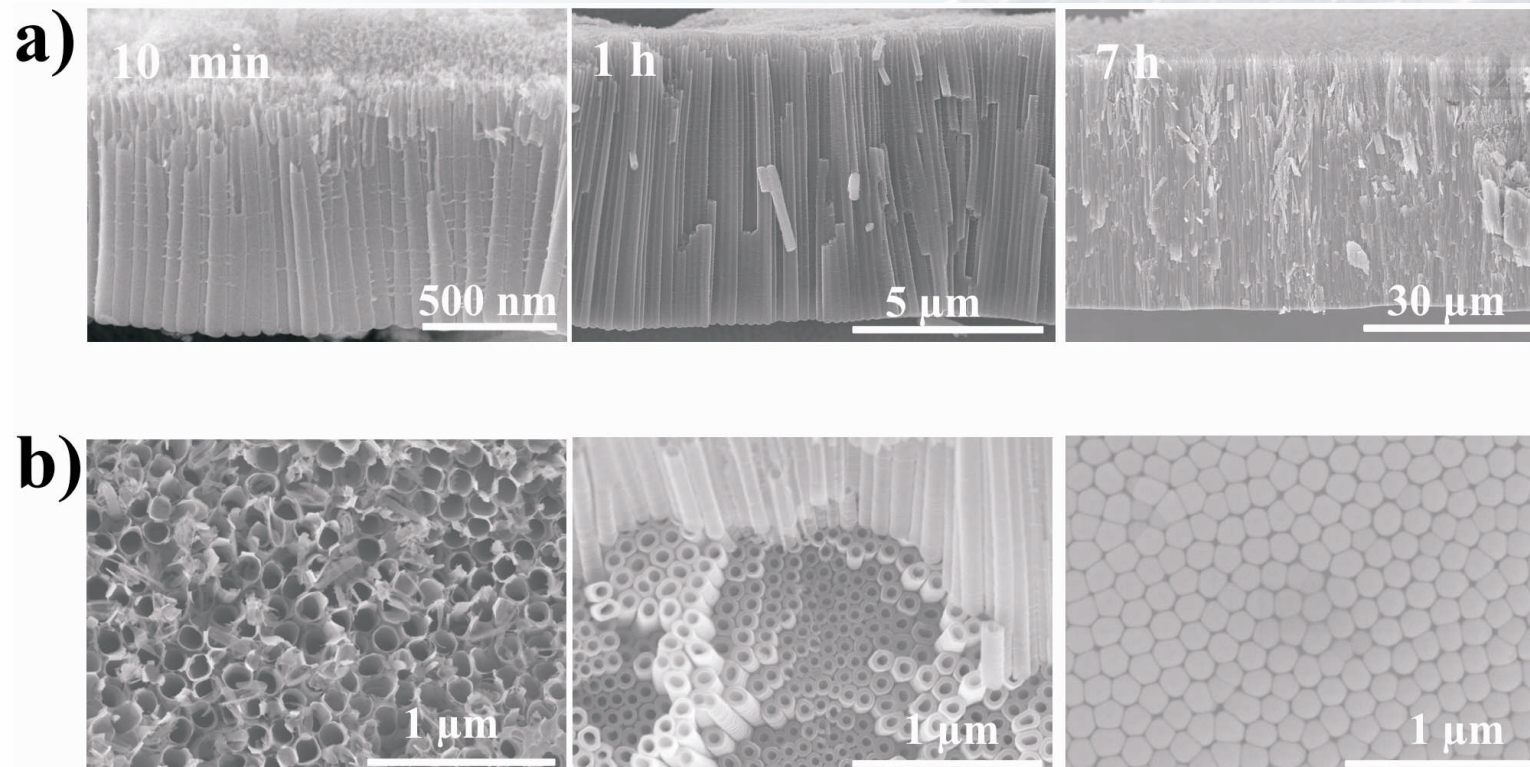
XPOT light source
control potentiostat
(Photo sensor hidden
behind the PECC)



Function principle of CIMPS/CIMVS

Introduction (2)

Properties of the TiO_2 Nano-Tubes Prepared





- The Pt on FTO counter electrode causes most of the efficiency decline with time of the TiO_2 nanotube based thin film DSSC.
- A new equivalent circuit approach allowed this clear assignment.
- The new equivalent circuit model can be confirmed by the TRIFIT procedure fitting three different types of transfer function, EIS-, CIMPS- and CIMVS, all from the same system state of the sample.
- A model, which is able to fit EIS-, CIMPS- and CIMVS together avoids the ambiguity of isolated EIS measurements and is therefore definite with high probability.
- The characterization of nanotube based thin film DSSC by dynamic methods should be continued with higher sample count and systematic series measurements over time and load.

Thank You for Your Attention!