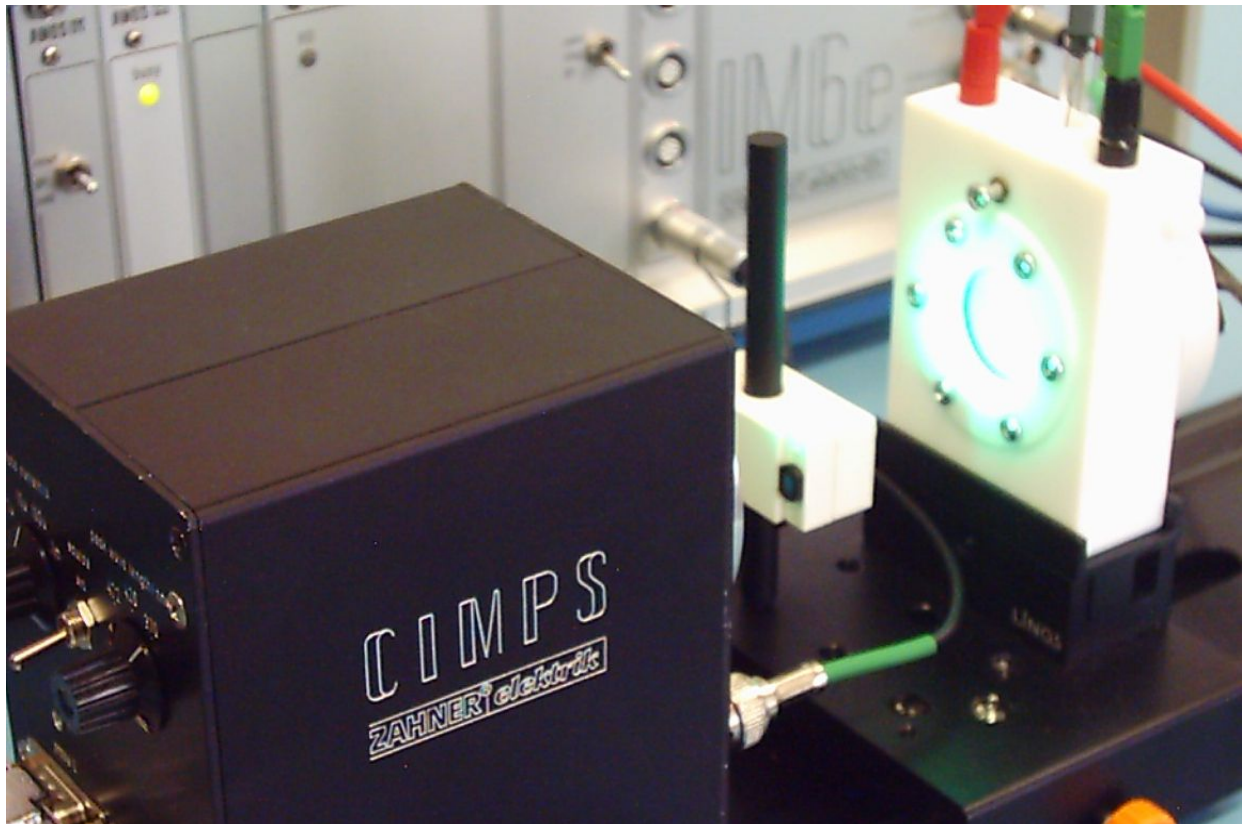


Controlled Intensity Modulated Photo Spectroscopy

CIMPS

Combines electrochemical impedance and dynamic photocurrent / potential measurements

LED-based dynamic measurements on photo-active systems



solar cells
semiconductors
photo-induced chemical reactions
conducting polymers

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M E S S Y S T E M E

Principles

Light induced processes like photosynthesis are of fundamental significance in the world. In technique, the “photo-electric effect” occurring at illuminated interfaces like semiconductor junction barriers is of big importance. Here, the electric potential and the current flowing at the interface site, are depending on the illumination. Light intensity with photo-voltage on the one hand and with photo-current on the other hand are building two typical force-response couples. The analysis of the transfer function (response function divided by the force function) can give important information about the static and the dynamic properties of the photo-electric effect and its mechanisms in detail.

Mainly the two transfer functions

photo-voltage efficiency = photo-voltage / intensity
and **photo-current efficiency = photo-current / intensity**

are of interest. Usually, they have to be determined in two slightly different electrical set-ups: the first one needs galvanostatic (or open circuit) control of the system under test, the second one needs potentiostatic (or short circuit) control.

The dynamic photo-effect transfer-functions can be determined in the frequency domain by modulating the light intensity in a broad frequency range, analogous to the EIS. This procedure is known in literature as *Intensity Modulated Photo Spectroscopy IMPS*. Often, a laser together with an electro-acoustical or electro-optical modulator and a frequency generation and correlation unit like an FRA or a Lock-In-Amplifier are used. Such arrangements are critical regarding the mechanical adjustment and the crosstalk caused by the high modulation voltages necessary. In the presence of small photoelectric effects they may cause measurement artefacts. Usually the absolute light intensity as well as the quality and depth of the modulation are not controlled automatically but show non-linearity as well as time and temperature drift. Furthermore, the highly focused light of a laser is not needed in many cases and beam expander lenses must be inserted into the beam to illuminate the electrodes under test, which have typical areas of some square millimetres to square centimetres.

Instead of lasers, the use of moderate focused Light Emitting Diodes (LED) can bring advantages. LEDs are much cheaper and can be modulated in intensity without causing excessive electrostatic or magnetic interference.

Practical

The Zahner CIMPS system based on LED arrays brings an additional advantage compared to the IMPS described in the literature: a control loop regulates light intensity and modulation and keeps it absolutely stable. The automatic comparison between set value and sensed intensity eliminates the influence of non-linearity, ageing and temperature drift. Furthermore, it allows the direct calibration of the light source in units of intensity (W/cm^2).

The CIMPS package consists of several components, working together in a plug & play application, including software and an overall calibration of the system. An ElectroChemical Workstation ECW IM6 or IM6e acts as a Frequency Response Analyser and as a support unit (Potentiostat / Galvanostat) for the cell under test. The IM-series workstations are renowned for their high precision, ease of use and comprehensive software. A slave potentiostat, driven by the IM6/IM6e system, controls amplitude and modulation of the light source over a wide range of frequencies.

An optical bench carries the housing of the light source with the integrated photo-amplifier and the slide with the photo-electrochemical cell. A photodiode sensor is mounted near the site of the cell’s light inlet, adjustable in height and angle. Depending on the application, you can chose from different types of light sources (see table).

With the Zahner CIMPS system the recording of a photo-electric transfer-function is as easy as an EIS or CV experiment. Five photo-electric methods are implemented into the standard IM software (see table). The unique USER-element feature of the SIM simulation & fitting software allows the scientist to include self-defined transfer functions into the simulation- and fitting services of SIM. This eases the analysis of the frequency dependencies occurring in photo-electric transfer functions.

On demand CIMPS can be delivered together with a photo-electrochemical cell. This cell is optimised for perfect optical as well as electrical characteristics and comes along with a Ag/AgCl reference electrode and a Pt counter electrode coil. The PTFE-based solid allows working in aggressive and non-aqueous electrolytes. Working electrode samples up to 20 mm diameter can be mounted easily.

Methods for the evaluation of the optical DC characteristics

Static photo-voltage curve $F_{UP} = U(P)$

Static photo-current curve $F_{IP} = I(P)$

IMPS related dynamic methods

Dynamic photo-voltage efficiency $H_{UP}(\omega) = \frac{U(t)}{P(t)}$, with $U(t) = \hat{U} \cdot e^{j\omega t + \varphi_u}$, $P(t) = \hat{P} \cdot e^{j\omega t}$

Dynamic photo-current efficiency $H_{IP}(\omega) = \frac{I(t)}{P(t)}$, with $I(t) = \hat{I} \cdot e^{j\omega t + \varphi_i}$, $P(t) = \hat{P} \cdot e^{j\omega t}$

Calibration routines

Dynamic light-source efficiency $H_{EP}(\omega) = \frac{P(t)}{E(t)}$, with $P(t) = \hat{P} \cdot e^{j\omega t + \varphi_p}$, $E(t) = E \cdot e^{j\omega t}$

- | | | | |
|------------|---|-----------------------|------------------------|
| <i>P</i> : | Luminous Intensity [W/cm ²] | $\hat{}$: | amplitude symbol |
| <i>U</i> : | Photo voltage [V] | ω : | angular frequency [Hz] |
| <i>I</i> : | Photo current [A] | φ : | phase shift [rad] |
| <i>E</i> : | Light source potentiostat set voltage [V] | <i>j</i> : | imaginary unit |

Electrochemical methods & utilities

- Electrochemical Impedance Spectroscopy EIS
- Impedance & Network Analysis, Simulation & Fitting
- EIS Series vs. parameter (time, potential, current, temperature, pH...)
- Impedance vs. parameter (time, potential, current, temperature, pH...)
- Stationary Current / Voltage Characteristics & Polarisation Measurements
- Cyclic & Linear Sweep Voltammetry
- Differential Pulse & Stripping Voltammetry
- Tast Polarography, Differential Pulse Polarography, Standard Addition Analysis
- Multi-Cell & Multi-Potentiostat measurements
- Arbitrary Current / Potential / Time Measurements (pulses, steps, ramps...)
- Universal Frequency Analysis, Fast Pulse & Transient Recording
- Universal Measurement Data Acquisition & Control
- Relaxation Voltammetry, Electrochemical Noise Analysis, High Current Interrupt
- Graphic, documentation & programming utilities ...

Colour	Dominant Wavelength (nm)	Spectral Half-Width (nm)	Maximum Flux (lm) or Output Power (mW)	Viewing Angle 2-θ½ (degree)	Part Code Number
White	(3300K)		14		WL01
UV	370	10	30 mW	30	UVZ01
UV	395	20	150 mW	10	UVR01
Royal Blue	455	20	55 mW	10	KBL01
Blue	470	25	4	10	BLL01
Cyan	505	30	14	10	CYL01
Green	530	35	14	10	GRL01
Amber	590	14	23	10	GEL01
Red Orange	610	20	40	10	ORL01
Red	625	20	30	10	RTL01
IR	880	30	600 mW	20	IRR01
Royal Blue to UV switchable	370	10	10 mW	30	BUVZ01
	400	20	15 mW	30	
	428	20	5 mW	30	

Supported wavelength range	User selectable, see table 1
<u>with PP210 potentiostat unit as light source supply:</u>	
Frequency range	10 µHz – 100 KHz
Supply output range for LED light source	±10 A, ± 20 V
<u>with EPOT potentiostat unit as light source supply:</u>	
Frequency range	10 µHz – 250 KHz
Supply output range for LED light source	± 0.2 A, ± 10 V
<u>Photo-electrochemical cell:</u>	
Width x depth x height	60 x 25 x 80 mm
Optical window diameter	20 mm
Optical window material	BK4 or Quartz
Working electrode diameter	Max 20 mm
Solid material	Teflon
Reference electrode	AgAgCl
Counter electrode	Pt coil