and generation of VUV radiation *via* 4-wave mixing in rare-gases. We also have a Nd:YAG laser pumped lithium niobate OPO that produces tunable IR radiation from 1.2 to 3.5 μ. For characterization of these laser sources we employ pulsed wavemeters and a pulsed spectrum analyzer. We also have two pulsed TEA CO_2 lasers which produce 1.5 J per pulse at 20 Hz.

For ultrafast time-resolved measurements, we employ a femtosecond laser system containing a cw Ar-ion-laser pumped Ti:Sapphire laser and a Nd:YAG pumped chirped pulse amplification (CPA) system in a temperature- and dust-controlled laboratory. At a repetition rate of 1 kHz the system produces 100 fs laser pulses at 1 mJ pulse energy at 800 nm. For diagnostics we use a scanning autocorrelator and

a Frequency-Resolved Optical Gating (FROG) detector. Tunable visible and IR radiation is created by an optical parametric amplifier which delivers *ca.* 0.1 mJ at 1.6 μ and 1 kHz repetion rate of the pump laser. For the combination with the nanosecond laser pulses, a 20 Hz Nd:YAG pumped amplifier is set up to boost the energy of the Ti:Sapphire pulses to a level of *ca.* 5 mJ per pulse. We also use a Nd:YAG pumped dye amplifier chain seeded by white light from a continuum generation unit.

Some Recent Publications

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Research at the Laboratory for Photonics and Interfaces

(Institute of Physical Chemistry II)

Prof. Dr. **Michael Grätzel***

1. Introduction

Laboratory for Photonics and Interfaces (LPI), the second chair of the Physical Chemistry Institute will soon be completing 20 years of its existence under the direction of Prof. *Michael Grätzel*. Set up initially as a chair devoted to study of fundamental aspects of photochemical processes in solution, the research interests of the group have expanded significantly over the years. Today a wide spectrum of research projects are studied covering areas of photochemistry, photoelectrochemistry, colloids, catalysis (thermal, photo-, and electro-), and surface science. The knowledge and the expertise gained in the first decade working on colloids, membranes and thin films have lead to current efforts devoted to photo-, electro-, and photoelectrochemical systems based on nanocrystalline materials. Significant advances in the fields of colloid and sol-gel chemistry in the last two decades now allow fabrication of micro- and nano-sized structures using finely divided monodispersed colloidal particles [1–4]. Nanocrystalline semiconductor films are constituted by a network of mesoscopic oxide or chalcogenide particles such as TiO_2, ZnO, Nb_2O_5, WO_3, Ta_2O_5, CdS, or $CdSe$, which are interconnected to allow electronic conduction to take place. The pores between the particles are filled with

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Michael Grätzel was born in 1944 in Germany. Studied Chemistry at the Free University of Berlin, from where he obtained 'Habilitation' in 1975. Doctoral thesis research (on fast kinetic studies of radiation-induced formation of radicals in solution, Tech. Univ. of Berlin) was carried out at the *Hahn-Meitner* Institute, Berlin, and this was followed by a two-year stay at the Radiation Laboratory of the Univ. of Notre Dame, Indiana, USA. Has been a professor at EPFL since 1977. Served as Head of the Dept. of Chemistry from 1983–1985 and from 1991–1993. Author of over 500 journal publications, two books, two edited monographs, and 10 patents. Has been a visiting Professor at the Univ. of California, Berkeley, and National Renewable Energy Research Labs (NREL), Colorado, USA; Visiting lecturer at Univ. of Texas at Austin. Fellowship of the Japanese Society for the Promotion of Science. Member of editorial board of several journals and acts as consultant to international industrial corporations. Was awarded recently a honorary Doctor of Science (D.Sc. honoris causa) by Uppsala Univ. in Sweden.

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a semiconducting or a conducting medium, such as a p-type semiconductor, a hole transmitter or an electrolyte, forming a junction of extremely large contact area. In this fashion, the negatively and positively charged contact of the electric cell become interdigitated on a length scale as small as a few nanometers.

Nanostructured materials offer many new opportunities to study fundamental processes in a controlled manner and this in turn lead to fabrication of new devices. The unique optical and electronic features of these are being exploited to develop opto-electronic devices such as photoelectrode in solar cells, photochromic displays/switches, optical switches, chemical sensors, intercalation batteries, capacitor dielectrics/super-capacitors, heat-reflecting and UV-absorbing layers, coatings to improve chemical and mechanical stability of glass, etc. In some recent articles [5–7], we have outlined some of these novel applications. In the following paragraphs, we present a very brief outline of different projects that are currently under scrutiny.

2. Nanocrystalline Injection Solar Cells

Nearly two-third of the research efforts of LPI are focused towards development of a dye-sensitized photovoltaic cell for the direct conversion of sunlight to electricity [8–14]. Conventional solar cells convert light into electricity by exploiting the photovoltaic effect that exists at semiconductor junctions. They are thus closely related to transistors and integrated circuits. The semiconductor performs two processes simultaneously: absorption of light, and the separation of the electric charges ('electrons' and 'holes') which are formed as a consequence of that absorption. However, to avoid the premature recombination of electrons and holes, the semiconductors employed must be highly pure and defect-free. The fabrication of this type of cell presents numerous difficulties, preventing the use of such devices for electricity production on an industrial scale.

In contrast, the solar cells developed in our group at the Swiss Federal Institute of Technology work on a different principle, whereby the processes of light absorption and charge separation are differentiated. The nanocrystalline injection solar cell consists of two conducting glass electrodes with a redox electrolyte separating the two. On one of these electrodes, a few-micron-thick layer of TiO_2 is deposited using a colloidal preparation of monodis-

persed particles of TiO_2. The compact layer is porous with a high surface area, allowing monomolecular distribution of dye molecules. Due to their simple construction, the cells offer the hope of a significant reduction in the cost of solar electricity. Light absorption is performed by a monolayer of dye adsorbed chemically at the semiconductor surface. After having been excited by a photon of light, the dye – usually a transition-metal complex whose molecular properties are specifically engineered for the task – is able to transfer an electron to the semiconductor (TiO_2) (the process of 'injection'). The electric field inside the bulk material allows extraction of the electron. Positive charge is transferred from the dye to a redox mediator ('interception') present in the solution with which the cell is filled, and thence to the counter electrode. Via this last electron transfer, in which the mediator is returned to its reduced state, the circuit is closed. The theoretical maximum voltage that such a device could deliver corresponds to the difference between the redox potential of the mediator and the Fermi level of the semiconductor.

2.1. The Porous Nanostructured Film

Titanium dioxide represents the semiconductor of choice for the production of nanostructured films. It is itself insensitive to visible light by virtue of the width of the forbidden band (3.2 eV) and only begins to absorb in the near ultraviolet. However, it can be photosensitized by a wide range of dyes, certain of which allow an incident light-to-electricity conversion approaching unity. TiO_2 is a cheap material and used widely as a white pigment in paint or paper. Its lack of toxicity allows it to be employed as an abrasive in toothpaste or for other cosmetic products. The production of nanostructured films on glass substrates is performed by straightforward screen-printing of a colloidal suspension of TiO_2 (produced by sol-gel methods), followed by a curing step at 450°, which causes the particles to fuse with each other, thus assuring the solidity of the whole film. The nanometer-scale of the particles (10–30 nm) confers on the film a roughness factor of ca. 100 per μ thickness. In this way a 10-μm-thick, nanostructured layer possesses an internal surface a thousand times greater than a dense, flat film.

The absorption of light by a monolayer of dye is always destined to be weak. A respectable photovoltaic efficiency cannot therefore be obtained by the use of a flat semiconductor surface but rather by use of a porous nanostructured film of very high surface roughness. When light

penetrates the photosensitized, semiconductor 'sponge', it crosses hundreds of adsorbed dye monolayers. The nanocrystalline structure equally allows a certain spreading of the radiation. The end result is a greater absorption of light and its efficient conversion into electricity.

Despite the heterogeneous nature of the semiconducting material, the diffusion of electrons in the bulk matter towards the supporting conductor occurs with almost no energy loss. The recombination between the electron which is injected into the conduction band of the semiconductor and the hole that remains on the oxidized dye is effectively very slow, compared to the reduction of the latter by the mediator in solution. Furthermore, electron-hole recombination in the semiconductor which seriously affects the efficiency of classic photovoltaic cells does not occur in this case, due to the fact that there is no corresponding hole in the valence band for the electron in the conduction band. As a result, the efficiency of the cell is not impaired by weak illumination, e.g., under a cloudy sky, in contrast to what happens with classical systems.

It should be emphasized that the performance of the solar cell is intimately based on the material content, chemical composition, structure and morphology of the nanoporous oxide layer [15–24]. Fortunately, the colloid chemistry has advanced tremendously in the last two decades [25][26] that it is now possible to control the processing parameters such as precursor chemistry, hydrothermal growth temperature, binder addition and sintering conditions and optimize the key parameters of the film viz., porosity, pore size distribution, light scattering, electron percolation. For efficient dye distribution, the surface area of the membrane film must be large. It is known that smaller the particle size, larger will be the surface area of the film. For the fast regeneration of the oxidized dye and charge transport, the redox electrolyte must be able to penetrate the pores efficiently and be present in places where the dye penetrates. Larger the particle size, the larger will be the porosity of the layer. Larger particles also scatter the incident radiation more effectively and this has been found to be a positive factor in enhancing the red-light response of the sensitizer. Preparation and characterization of monodispersed colloids of different oxides such as TiO_2, Nb_2O_5, ZnO, Ta_2O_5, Fe_2O_3 are pursued in this context. The colloids are used for deposition as nanocrystalline films of thickness of 0.5–10 μm by doctor blade technique or by screen printing. The films are examined

alone or in the presence of dyes by several techniques such as X-ray diffraction, electron microscopy, luminescence, and *Raman* spectroscopy.

2.2. *The Dye*

The dye represents the key element of the cell. The molecular engineering of the dye needs to take into account the following: a) tuning of spectral properties (MLCT absorption in the case of polypyridine complexes of Ru) so as to ensure maximal visible light absorption; b) tuning of redox properties in the ground and excited state to ensure fast charge injection and regeneration of the oxidized dye; and c) introduction of anchoring groups to ensure uniform (monomolecular) distribution of the dyes on the oxide surface and to promote electronic coupling of the donor levels of the dye with the acceptor levels of the semiconductor; and d) choice of counterions and degree of protonation (overall charge) to ensure sufficient solubility in organic, aqueous solvents and control of proton and water content in the pores during the loading of the dye. The dye must also be capable of displaying an excellent stability that allows accomplishment of the thousands (or even millions) of excitation-oxidation-reduction cycles which must be performed during the required 20-year-operational life-time of the cell.

In our studies, we have examined a number of 'transition-metal complexes' and 'organic dyes' as potential candidates. Organic dyes which have been tested to date are generally degraded after only a few thousand cycles and consequently cannot be considered as viable options for the moment. Polypyridines, porphyrins, and phthalocyanines are nature choice for the ligands, since these ligands are known to chelate to a large number of metals, the resulting complexes are stable in several oxidation states and exhibit rich photochemistry. Towards implementing the criteria listed in the previous paragraph, a large number of complexes which strongly absorb visible light have been synthesized and their performance in solar cells assessed.

Polypyridine complexes exhibit strong visible light absorption arising from charge-transfer transitions from filled d orbitals (t_{2g}) of the central metal ion (Ru) to the empty π^* orbitals of the bipyridine ligand. The MLCT excited states are fairly long-lived in fluid solutions and undergo efficient electron-transfer reactions. In the last two decades, a vast amount of literature has grown on the photophysics and photochemical properties of these com-

plexes [27–29]. Quantitative analysis of the spectral, electrochemical, and photophysical properties of several hundred complexes have led to clear understanding of the CT transitions, that it is now feasible to tailor-made complexes with desired properties. Examples of Ru-complexes that work efficiently as photosensitizers are [Ru(dcbpy)$_2$(NCS)$_2$] and [Ru(PO$_3$-terpy)(Me$_2$bpy)(NCS)] where dcbpy = 4,4'-dicarboxy-2,2'-bipyridine; PO$_3$-terpy = 4'-phosphonato-2,2':6',2"-terpyridine and Me$_2$bpy = 4,4'-dimethyl-2,2'-bipyridine [8][9]. Current efforts on dye design focus on dyes that have significant absorption in the red, near-IR region of the solar spectrum. Phthalocyanines are interesting candidates in this context. A potential application of IR-light-absorbing dyes is in 'smart windows' – windows that are transparent to visible light yet can absorb significant IR radiation to generate electricity during the daytime.

2.3. *The Redox Mediator*

For stable operation of the solar cell and maximal power output, the oxidized dye must be reduced back to the ground state as rapidly as possible by a suitable electron donor. Since the maximum photovoltage obtainable is related to the position of the mediator redox potential, it is preferable to choose a couple whose potential is as close to the $E(S^+/S)$ as possible. As with the charge injection step, the choice of the mediator should be such that there is enough driving force (≥ 250 mV) for the dye reduction step to have optimal rate. Thirdly, for stable performance of the solar for months, the redox couple must be fully reversible, no significant absorption of the visible light region and stability in the oxidized, reduced forms. The iodide/triiodide couple is currently being used as the redox mediator of choice. The electrolyte containing the mediator could be replaced by a p-type semiconductor, e.g., cuprous thiocyanate, CuSCN [30], or cuprous iodide, CuI [31], or a hole-transmitting solid, such as the amorphous organic compounds used in electroluminescence devices. These alternative options are being examined in our laboratory. Replacement of organic electrolytes by room-temperature-molten salts such as 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imidee provides additional flexibility in the solar cell design [32].

2.4. *The Counter-Electrode*

In our studies, we employ a F-doped SnO$_2$ as the conducting glass electrode(s). Such electrodes are known to be poor

choice for efficient reduction of iodide. To reduce the overvoltage losses for the reduction of the mediator (I$_3^-$ + 2 e$^-$ → 3I$^-$), a very fine Pt-layer or islands of Pt (5–10 µg/cm^2) is deposited onto the conducting glass electrode. This ensures high exchange current densities at the counter-electrode and thus the processes at the counter electrode do not become rate-limiting in the light-energy-harvesting process. By developing a new mode of Pt deposition, we have engineered an extremely active electrocatalyst attaining exchange current densities of > 0.1 A/cm^2 at very low Pt-loading. This electrocatalyst is very stable and does not show long-term anodic corrosion as was observed in the case of Pt deposits produced by conventional sputtering or galvanic methods.

2.5. *Charge Transport/Electron Percolation within the Film*

Optimization of the solar cell requires a thorough understanding of various electrochemical and electron-transport processes involved. Basic studies are being undertaken to probe some of these fundamental processes directly [33][34]. As illustrations, two processes can be cited. Electron percolation refers to the process by which the electrons into the semiconductor hop through the colloidal oxide particles and arrive at the collector conducting glass electrode [35]. An ideal description of the film would be as a collection of large number of particles interconnected with large pores in between – that electrons injected onto any of the constituent particle can traverse through the network and reach the collector/back electrode. High IPCE values (in excess of 85%) indicate that the electron percolation in the nanoporous films can be a very efficient process. From a fundamental point of view, this is one of the most intriguing process amongst many that takes places in the solar cell.

Dark currents is another area. The oxide layer is an inter-connected network of particles with high porous interior. The dyes can penetrate everywhere and adsorb over a large surface area. The redox mediator also must penetrate the same domain so as to be present in the immediate vicinity of the photosensitizer. If the redox mediator gets to the back contact, dark currents arise from the reduction of the redox mediator by the collector electrode with the oxide layer (2 e$^-$ + I$_3^-$ → 3I$^-$). In principle, this charge recombination can occur at the surface of not only TiO$_2$ but also on SnO$_2$ because of the porous nature of the TiO$_2$ film. In reality, the reaction occurs at the TiO$_2$ particle/redox electro-

lyte interface due to the relatively large surface area of the nanocrystalline film. In order to reduce the dark current, an oxide underlayer is deposited. Alternatively, exposure of the dye-coated electrode to a solution of a pyridine derivative (donor) such as 4-(tert-butyl)pyridine was found to improve dramatically the fill factor (ff) and the open-circuit voltage (V_{oc}) of the device without affecting the short-circuit photocurrent (i_{sc}) in a significant fashion.

2.6. Efficiency of the Solar Cells

The efficiency of photosensitization by the dye is assessed in the form of incident photon-to-current conversion efficiency (IPCE) values. The IPCE value is the ratio of the observed photocurrent divided by the incident photon flux, uncorrected for reflective losses for optical excitation through the conducting glass electrode. The IPCE value can be considered as the effective quantum yield of the device and it is the product of three key factors: a) light-harvesting efficiency LHE (λ) (depend on the spectral and photophysical properties of the dye); b) the charge injection yield ϕ_{inj} (depend on the excited-state redox potential and the lifetime); and c) the charge collection efficiency h_{el} (depend on the structure and morphology of the TiO$_2$ layer). With the Ru complexes shown above, the IPCE values in excess of 85% can be obtained in the region corresponding to the absorption maximum of the Ru complexes (400–550 nm). Near unit values of IPCE suggest that, in the present case, the charge injection and charge collection steps operate at optimal efficiencies.

The overall efficiency (η_{global}) of the photovoltaic cell can be obtained as a product of the integral photocurrent density (i_{ph}), the open-circuit photovoltage (V_{oc}), the fill factor (ff) and the intensity of the incident light (I_s). In typical lab experiments, solar cells with irradiation area of 1–2 cm^2 are made and tested. The photocurrent measured under 96.4 mW/cm^2 simulated solar light (AM 1.5, corresponding to a solar elevation of 42° to the horizon) and the open-circuit voltage are equivalent to 18.3 mA/cm^2 and 0.72 V, respectively. With a fill factor in the range of 0.70, the overall white light to electrical conversion efficiency can be obtained around 10%.

3. Dynamics of Light-induced Interfacial Electron-Transfer Processes

One of the long standing research interest of the group has been fundamental studies of photoinduced electron-transfer processes, particularly at the interfaces [36][37]. Fast kinetic/time-resolved spectroscopic studies are applied to metal complexes and organic dyes in solution, adsorbed onto a colloid or electrode or in aggregated form. In systems involving semiconductor colloids, particulates or translucent/nanocrystalline films, by appropriate choice of excitation wavelength, optical excitation can be confined either to adsorbed dyes or within the forbidden bandgap. In this manner, electron-transfer reactions involving electrons and holes photogenerated within the semiconductor with chemical species present in solution can be studied and also reactions of electronically excited states of adsorbed dyes [38–41]. These studies are of particular relevance in our understanding of the working of the dye-sensitized solar cells and can provide important clues towards improving their performance.

For efficient processing of charge separated products, it is of interest to develop systems where there is orders of magnitude difference in the forward and back electron transfer rates. Fortunately, in the present case, these rates differ by more than a million. The charge injection step occurs in few picoseconds or less but the back reaction of the electrons of TiO$_2$ with the oxidized Ru complex is extremely slow, occurring typically in the microsecond time domain [11][41–47]. Depending on the dye and associated energetics, back electron transfer rates have been found to vary by more than six orders of magnitude. Analysis of these processes taking into account excited state and hot carrier relaxation steps as well as trapping of charges on localized states, allow estimation of reorganization energies and electronic coupling matrix elements.

Charge-transfer reactions have almost exclusively been studied with donor-acceptor systems in a medium (polar or nonpolar solvent, frozen matrix, protein, ...). Electron-transfer reactions in condensed media belong to a large class of nonradiative processes that imply conversion of electronic excitation into vibrational energy. Recent theoretical and experimental advances are presently questioning the dominant role attributed to medium coupling in charge transfer. In the present cases of electron-transfer reactions at the surface of solids as well as in supramolecular assemblies, only a minor role of solvent is expected, quantum effects (nuclear tunneling, inner-sphere vibrational reorganization become very important. Dependence of the nonradiative electronic processes vs. parameters such as the temperature, nature of the medium, geometry of the system, free energy of the reaction, mode specific reorganization energies, and the excitation wavelengths are scrutinized. Data are analyzed using semi-classical theories to reach a better understanding of the role of vibrational modes in the dynamics of intermolecular and interfacial fast electron-transfer processes.

4. Nanocrystalline Intercalation Batteries

In the so-called 'rocking chair' batteries, electric power generation is associated with migration of Li$^+$ ions from one host, i.e., TiO$_2$-constituting anode to another host electrode, i.e., NiO$_2$/CoO$_2$ or MnO$_2$ (cathode). The materials are used in the form of micron-sized particles compressed pellets mixed with carbon and a polymeric binder. The morphology of the electrodes are such that large pores/channels present therein allow reversible insertion of Li and extraction into and from the lattice. Studies involving mesoporous TiO$_2$ films [48] [49] have shown that efficient, reversible and rapid intercalation of lithium occurs due to very short diffusion time for lithium ions in these mesoscopic oxide structures. A standard size R921 coin cell has been developed supplying 4–4.5-mAh corresponding to 50-mAh/g capacity which compares well with the rocking chair battery having a carbon anode. These findings provide a very promising basis for the development of a new type of rechargeable battery.

5. Electrochromic and Photochromic Displays

Electrons are majority carriers on n-type semiconducting oxides and hence injection of electrons from outside into the junction drives the nanocrystalline oxide film into the accumulation region. Accumulation of conduction-band electrons in the oxide leads to electrochromic effect, viz. development of a broad absorption in the visible and near-IR region [50]. Electrochromic switching of mesoscopic films occurs rapidly due to ready compensation of the injected space charge by ion movement in the electrolyte present in the pores.

Viologens form a group of redox indicators which undergo drastic color changes upon oxidation/reduction. The reduced form of methyl viologen, e.g., is deep blue, while the oxidized form is colorless. Efficient reduction of anchored viologen

compounds by conduction-band electrons of TiO_2 can be used for the amplification of the optical signal. The amplification is due to orders of magnitude higher molecular extinction coefficients of these relays. Upon electroreduction, transparent nanocrystalline film of TiO_2 containing viologen develop strong color and the film can be decolorized by reversing the potential. Varying the chemical structure and redox potentials of the viologens, it is possible to tune the color and hence build a series of electrochromic display devices [51][52]. Such surface derivatized nanocrystalline devices accomplish a performance which in terms of figure of merit, i.e., the number of charges required to achieve an optical density change of one is already competitive with conventional electrochromic systems and hence show great promise for practical applications.

6. Photo- and Electrocatalytic Degradation of Pollutants and Pesticides

This project has, as the goal, development of methods of decontamination of toxic, non-biodegradable pollutants by catalytic and photocatalytic methods. Inefficacity of the classical methods to refractory pollutants is the reason for the chronic contamination of the environment and the associated increase in the ecotoxicological effects. Towards rendering industrial wastes compatible with environment, our project attacks the source of certain pollutants, particularly aromatic sulfones, phenols, nitrophenols, and (4-nitrotoluene)sulfonates. The objectives are acquisition of fundamental aspects on one hand and integration of photocatalytic (solar) or electrochemical with biological treatment.

Bandgap excitation of a semiconductor such as TiO_2 leads to generation of strong oxidant (holes) and reductants. In high surface area particulate suspensions of TiO_2, these photogenerated redox species are rapidly converted to hydroxyl radicals and other oxidants. Alternatively, strong oxidants can be generated in solution in Fenton-type reactions. Usage of electrocatalysts also allow controlled generation of oxidants. The radicals produced by any of the above methods can then attack and destroy organic pollutants. These photocatalytic or electrochemical treatments modify the structure of the pollutant, rendering it less toxic and/or more easily biodegradable. Within the framework of biodegradation of xenobiotics, the project represents a new contribution for the degradation of aromatics, particularly as it concerns treatment of used toxic waters. Reactors capable of rending the solution biocompatible via a rapid catalytic treatment are being developed. The kinetics of biodegradation is followed and the experimental data allow improvement of the dynamics of reactors in the biodegradation of organic pollutants. An extended outline of this project has been published recently [53] (in the earlier issue of CHIMIA 3/96 devoted to 'Catalysis in Switzerland') and readers are referred to this for details.

7. Technology of High-Temperature Solid Oxide Fuel Cells

Fuel Cells convert chemical energy into electricity with high efficiency, not limited by Carnot cycle. The fuel (H_2) and the oxidant (air) are fed continuously to the anodic and cathodic compartments, respectively, operating at relatively high temperatures of 800–1000°. Despite its high operating temperature, solid oxide fuel cells (SOFC) have the possibility of using hydrocarbons such as methane as fuel. This has the advantage of avoiding hydrogen storage and liquid electrolyte leakage, in addition to fast electrode kinetics. Research efforts in Lausanne are directed towards elaboration of materials and processes for the fabrication, put into service and functioning of solid oxide fuel cells operating at 1000°, establishment of hydrocarbons as fuels and electrocatalysis and other means to reduce the operating temperature. An extended outline of this project has been published recently [54] (in the earlier issue of CHIMIA 3/96 devoted to 'Catalysis in Switzerland') and readers are referred to this for details.

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Laboratoire d'Electrochimie

Prof. Dr. **Hubert H. Girault***

The Laboratoire d'Electrochimie was created in 1992 after the dissolution of the Institut de Radiochimie and Electrochimie. The Laboratoire is now composed of *ca.* 20 members and is led by Prof. *Hubert Girault.*

The Laboratoire is active primarily in the study of **charge-transfer reactions across polarized liquid/liquid interfaces.** This field of electrochemistry is a rather new field and is sometimes called 'Electrochemistry without electrodes'. Indeed, contrary to classical electrochemistry concerned with electron-transfer reactions at the surface of a solid electrode, liquid/liquid interfaces, such as the interface between water and 1,2-dichloroethane, are molecular interfaces. In the case of boundaries between electrolyte solutions, these interfaces can be polarized and two back

to back space charged regions are used to generate a difference of *Galvani* potential between the two adjacent electrolyte solutions. This polarization of the interface yields an interfacial electric field which in turn can be used as a driving force for charge-transfer reactions. The charge-transfer reactions taking place can be divided into three types: ion transfer, assisted ion transfer by complexation and heterogeneous electron transfer (see *Fig.*).

Research at the Laboratoire d'Electrochimie is aimed at a better understanding of the interfacial structure and at unveiling the mechanisms of charge-transfer reactions.

Structural studies have been carried out using **Surface Second Harmonic Generation.** Indeed, nonlinear optical techniques are the only spectroscopic methods which are inherently surface-specific and therefore allow a direct probing of the orientation and relaxation of molecules in the nanometer-thick interfacial region [1]. For example, we have studied the orientation and solvation of phenol, *p*-nitrophenol and *p*-propylphenol at the air/water and hexane/water interface and showed

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Hubert H. Girault was born in France in 1957. In 1979, he graduates from the Ecole Nationale Supérieure d'Electrochimie et d'Electrométallurgie de Grenoble and goes to Southampton (England) to study the structural properties of liquid/liquid interfaces. After a Ph.D. in 1982, he remains in Southampton as a postdoctoral research fellow and undertakes a research programme of charge transfer across polarized liquid/liquid interfaces. In 1985, he becomes Lecturer of Physical Chemistry at Edinburgh University (Scotland) and starts a research group which specializes in the design and fabrication of electrochemical sensors. In 1989, he creates the company *Ecossensors* which pioneered disposable sensors for heavy-metal analysis. In 1991, *Ecossensors* received an award for technological merit from the Department of Trade and Industry. In 1992, he joins the Ecole Polytechnique Fédérale de Lausanne to take the Chair of Electrochemical Kinetics. The activities of the research group range from the application of nonlinear optics to the development of biosensors.
Hubert Girault is also Directeur de la bibliothèque commune de Chimie et de Pharmacie de Lausanne, Directeur de la collection Chimie des Presses Polytechniques Universitaires Romandes, and editor of the Preliminary Notes of *Journal of Electroanalytical Chemistry.*