Introduction

Photoelectrochemical (PEC) water-splitting is one of the many routes to hydrogen production (refer to Figure-1). PEC cells use semiconductor-based, photoactive electrodes that are immersed in an aqueous electrolyte or in water in order to form a liquid junction. In their simplest form, they may be described as integrated, or monolithic, photovoltaic-electrolytic water-splitting devices. A wide range of PEC and photocatalytic water-splitting processes are being investigated around the world. The IEA-HIA has been encouraging research & development (R&D) on PEC water-splitting since the late 1970ies, with Annex-20 “Hydrogen from Waterphotolysis” combining collaborative efforts among 21 expert R&D groups from 7 different countries.

Figure-1: Water-splitting as part of the many routes to hydrogen production (SPF-Rapperswil).

Annex-20 aims to develop highly efficient and stable photoelectrode/photicatalysis materials and associated system solutions for PEC water-splitting. The ultimate goal is to achieve sta-
ble PEC device performance with a Solar-To-Hydrogen (STH) efficiency of 7-10%. This report summarises the R&D progress made by the experts of Annex-20 during 2006. 3 expert meetings were held during 2006 (Lyon, France; Uppsala, Sweden; Tokyo, Japan).

R&D Progress

The main R&D efforts of Annex-20 throughout 2006 concerned the development of more advanced photoelectrode materials for solid-state PEC devices and the research on 2-reaction photocatalyst powders, used for PEC water-splitting when applied as suspensions in ponds. Some of the main progress reported on materials engineering, on demonstration systems and on combinatorial chemistry equipment is summarised as follows:

**Hematite (Fe$_2$O$_3$) Photo-Anodes**

While the performance enhancing effect of anion doping of hematite ($\alpha$-Fe$_2$O$_3$) films (most importantly using p-type Zn(II) and n-type Ti(IV)) is well proven, it has become clear from detailed studies conducted at the Swiss Federal Institute of Technology (EPF-Lausanne) that such doping has also a major influence on the surface morphology (see Figure-2b). More specifically, Si-enriched surfaces have shown to lead to higher Incident Photon Current Efficiency (IPCE). However, it remains to be shown whether or not such Si addition constitutes proper lattice-doping or rather a kind of surface coating only. Nevertheless, according to the University of Geneva (Uni-Geneva), Si acts as a structure-directing agent (refer to Figure-2a).

In addition, dipping the highly nanocrystalline surfaces with noble metals such as Co was found to produce a performance enhancement of between 10-15%. Figure-3 illustrates this enhancement, showing the comparative current-voltage characteristics of Si-doped Fe$_2$O$_3$ in darkness and under simulated light, with and without Co-doping.

![Figure-2a: Ti (5%) and Zn (5%) doped Fe$_2$O$_3$ thin films by ultrasonic spray deposition (Uni-Geneva).](image)

![Figure-2b: Si-doped Fe$_2$O$_3$ thin films (“coli-flower”) by atmospheric pressure CVD (EPF-Lausanne).](image)

At the Commonwealth Scientific and Industrial Research Organisation (CSIRO), a new vacuum arc technique is being used to produce highly nanocrystalline Fe$_2$O$_3$ thin films. Alternatively, at the Technical University of Delft (TU-Delft), Fe$_2$O$_3$-nanorods have been manufactured by oxidation at around 800°C. Similarly at TU-Delft, nanorods have also been produced through electrodeposition of Fe on TCO glass substrates, with subsequent oxidation in air at 400°C only. As a direct result of the Annex-20 expert meetings that were conducted during 2006, specific efforts are underway to successfully dope Fe$_2$O$_3$ nanorods, followed by coating with a thin film of noble metals. Comparative in situ material analyses on photoanode samples received from Annex-20 expert groups will be done at various laboratories, including...
at the Atomic Energy Commission (CEA), France, and the University of Queensland (Uni-
Queensland), Australia, where new advanced PEC material analysis capabilities have been
established. Such nanosized substrate structures are beneficial for light trapping and elec-
tron conduction, most importantly for nanosized photoelectrode material with short diffusion
length and fast recombination of electrons and holes – such as with Fe$_2$O$_3$.

![Graph showing current-voltage characteristics of Si-doped Fe$_2$O$_3$](image)

**Figure-3:** Current-voltage characteristics of Si-doped Fe$_2$O$_3$ in darkness and under simulated sunlight at pH=13.6, showing the effects of film preparation and of Co-doping (1M NaOH) (EPF-Lausanne).

Although 2006 has seen significant progress with the development of Fe$_2$O$_3$ as a preferred n-
type photoanode material for tandem-cell PEC water-splitting devices, the key challenges
with this material remain to be its very short diffusion length together with a high hole-
electron recombination rate and a corrosion-stability across a wide pH range (preferably a pH
of 5-9 due to the ultimate aim of using seawater for PEC water-splitting). The overall per-
formance enhancement aim for Fe$_2$O$_3$ photoanode thin films of 4-5 mA/cm$^2$ (up from today's
2.2 mA/cm$^2$), however, remains well within reach of the Annex-20 program.

**Silver Chloride (AgCl) Photo-Anodes**

At the University of Bern (Uni-Bern), AgCl photoanode materials have been developed for a
PEC tandem system based on a conventional Si solar cell (a-Si:H/Pt) as photocathode. Using
zeolite monolayers as a substrate showed that much improved photoactivity is possible
due to significant enhancement of the active surface area of AgCl photoanodes and due to
zeolite acting as a buffer for the AgCl ions. For this reason microporous support materials
(eg. zeolite A and L – refer to Figure-4) are being tested in combination with mesoporous ox-
ide substrates (TiO$_2$ nanotubes, mesoporous WO$_3$ and Al$_2$O$_3$ membranes). Preliminary re-
sults show that the conductivity between the substrates and the AgCl particles need to be
much improved. It is not sufficient to allow fast reoxidation of the reduced silver species that
are produced upon illumination of the AgCl.
Titanium Dioxide (TiO$_2$) & Tin Oxide (ZnO) Substrates

Although TiO$_2$ is still regarded a highly desirable and therefore widely studied photoelectrode material due to its stability in water as well as its abundance, all efforts by the Annex-20 experts to tailor single-oxide TiO$_2$ for effective and stable photon performance beyond the UV light range (eg. via surface morphology, doping, etc.) were thus far not leading to satisfactory results. However, for the first time, detailed joint studies between Annex-20 experts from the Uni-Geneva and the National Institute of Advanced Industrial Science and Technology (AIST) proved that the electrode resistance and the amount of the photocurrent are actually controlled by the mass transport in the electrolyte and not by the electron transport across the network of TiO$_2$ particles. In addition, it was also found that operation of the nanocrystalline TiO$_2$ electrodes is clearly affected by the conductivity of the electrolyte. In view of the comparably large, inherent challenges with the development of TiO$_2$ electrodes, Annex-20 experts brainstormed about new options and concluded that mixed oxide TiO$_2$ (eg. titanates with strontium or iron) warrant detailed attention.

Finally, due to grain boundary advantages, TiO$_2$ nanotubes were confirmed at TU-Delft to act as better performing PEC substrates for nanosized PEC materials than nanoparticulate TiO$_2$. This concept of using nanotube or nanowire substrates has also been studied in detail by CSIRO using a variety of ZnO nanotubes, coated with thin layers of pure and doped Fe$_2$O$_3$ using a filtered arc technique (FAD). Clearly improved optical absorption and IPCE have been measured for such composite photoelectrode materials (refer to Figure-5).

Metaloxide Photo-Catalysts & Photo-Electrodes

Metal and mixed-metal oxides are mainly being studied as promising material options for photocatalytic, primarily powder-based PEC water-splitting. Within Annex-20, R&D on photocatalysts for water-splitting is meanwhile conducted only by expert groups in Japan and Korea. At Tokyo University of Science (Tokyo-US), NaBiO$_3$ powder confirmed to act as O$_2$-evolution photocatalyst from NaIO$_3$ aqueous solution under VIS light irradiation ($\lambda > 420$nm), hence working well as part of a 2-step water-splitting system using an I-/IO$_3^-$ redox mediator and a
coumarine-derivative dye-sensitized TiO$_2$ photocatalyst for H$_2$-evolution. The NaBiO$_3$ powder material is being characterized and optimized for PEC water-splitting.

For comparison, complex-metal photoelectrode materials such as InVO$_4$ or BiVO$_4$ are meanwhile judged as being of scientific interest but inherently inefficient for PEC water-splitting. Associated R&D efforts by Annex-20 experts in Europe (mainly TU-Delft) have stopped while Japanese R&D continues at the AIST as treatment with gold (Ag) ions resulted in performance enhancement.

Interesting, however, are recent breakthrough findings from the scientific field of ferroelectrics (perovskites). As one early example, at Pohang University of Science and Technology (POSTECH), metal-doped perovskites and composite photocatalyst powders (photocatalytic nanodiode (PCD) configuration), particularly n-Cds nano-particles deposited on the bulk of p-Ag$_2$GaS$_2$ particles, are showing good activity for H$_2$-evolution under VIS light from water containing Na$_2$S/NaSO$_3$ or H$_2$S dissolved into alkali-containing water. In addition, a new configuration with a conducting ohmic layer between p- and n-type semiconductors has been developed (WO$_3$/W/PbBi$_{1.9}$Ti$_{0.1}$O$_9$) by depositing the W-clusters over p-type perovskite base material, and later oxidizing the surfaces of these clusters to obtain n-type WO$_3$ overlayers (see Figure-6). Systematic PEC water-splitting tests are being conducted.

As an additional metal oxide example, Mo-Co alloy thin-films have been developed for H$_2$-evolution at the Korea Institute of Science and Technology (KIST). These films are showing good activity and, above all, high stability in strong alkaline electrolytes when combined with FeNiOx films for O$_2$-evolution (films have O$_2$ deficiency on surface). However, while the FeNiOx films themselves did indeed decrease the overpotential for O$_2$-evolution, they did not show high stability in the electrolyte solutions.

**PEC Demonstration Systems**

Two new PEC demonstration cells have been developed at Tokyo-US, namely: (i) a S-doped TiO$_2$ film photoanode and Pt cathode (steady-state photocurrent of 5 µA/cm$^2$ obtained from NaOH aqueous solution under VIS light), and (ii) a TiO$_2$ (anatase) photoanode with 2 black-dye TiO$_2$ solar cells as tandem PEC cell (2 series-connected DSC solar cells with $\eta=6.3\%$, Voc=1.4V, Jsc=8.2mA/cm$^2$, ff=0.53, active cell area 2 x 5mm wide and 25mm long). The latter one resulted in a STH energy conversion efficiency of 1.2%, which demonstrates a new record for a stable, all-TiO$_2$-based PEC device.
Combinatorial Chemistry

While at AIST the new PEC high-throughput screening system has been inaugurated, at the Colorado State University (Colorado-SU), encouraging progress was made with the development of the comparably simple, ink-jet-printer based high-throughput combinatorial method for PEC materials synthesis and analysis. This technique is being prepared for widespread application, with the aim to eventually use the help of science students worldwide. If coordinated well, the systematic development of a worldwide, web-based PEC materials library is being considered. The expert groups of Annex-20 see themselves as ideal partners to jointly advance this concept worldwide.

Participation

31 research experts from 7 Annex-20 member countries (Australia, France, Japan, Korea, Netherlands, Switzerland and USA) and 3 non-member countries (Germany, Mexico, Sweden) have participated in the 3 Annex-20 expert meetings conducted during 2006 (Lyon, France; Uppsala, Sweden; Tokyo, Japan). Additionally, researchers from Portugal, Spain and the United Kingdom maintained a high level of interest in PEC water-splitting work conducted through the Annex-20 program.

Collaboration

The R&D experts of Annex-20 maintain a worldwide network of information, people and knowhow exchange for PEC water-splitting. Most notable has this collaboration been during 2006 in the area of fundamental materials research and exchange of new material specimens.

In addition, European Annex-20 expert groups decided to jointly prepare for a PEC-focused, 4+3-year R&D program submission under the FP7 research program of the European Union. Thanks to the Swiss Federal Office of Energy (SOFE), it has been possible to secure some funding for the central Swiss coordination and preparation of this EU-FP7 submission.
Outlook

The 3-year collaborative R&D program of Annex-20 will finish at the end of 2007. The experts of Annex-20 will meet mid-year-2007 to critically review all progress made and to decide whether or not to apply to the Executive Committee of IEA-HIA for a 2-year extension of the program.

Recommended Reading

An extract of recent PEC publications from Annex-20 expert groups is provided as follows:


Vanga R., Currao A. and Calzaferri G.; “Gold and silver metal nanoparticle modified AgCl photocatalyst for water oxidation to O$_2$”; J. of Physics (in press).