FINAL TASK MANAGEMENT REPORT
Annex-14

"Photoelectrolytic Production of Hydrogen"
IEA Hydrogen Implementing Agreement

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1. Introduction

The collaborative Research & Development (R&D) program of Annex-14 has been focusing on the development of materials and systems for the photoelectrochemical (PEC) production of hydrogen.

Nine research groups from Japan, Sweden, Switzerland and the United States of America (USA) have been collaborating under Annex-14 since July 1999.

The 4.5-year program has been successfully completed toward the very end of 2003 to make room for Annex-20 ("Hydrogen from Waterphotolysis"), a new 3-year R&D program that is planned to comprise many more international R&D groups and to start in October 2004.

2. Objectives

The overall objective of Annex-14 was to significantly advance the fundamental and applied science in the area of PEC production of hydrogen over a period of three to five years.

More specifically and from a scientific point of view, research efforts aimed to focus on new semiconductor materials and structures, on photosensitive dyes, on integrated photovoltaics / electrolysis systems, and on novel single- as well as dual-bed reactor arrangements.

In addition, it was planned to attempt the evaluation and comparison of performance data regarding practical PEC system efficiency and device lifetime.

3. Accomplishments

Significant research progress has been made during Annex-14 in the areas of material science (semiconductor photoelectrodes, light absorption, photocatalyst stability and charge transfer) and systems development (monolithic multi-junction systems, two-photon tandem systems, dual-bed redox systems and monomaterial two-step systems), resulting in the demonstration of various laboratory-scale PEC water-splitting prototype devices.

The main scientific accomplishments of the collaborative R&D efforts conducted under the umbrella of Annex-14 include:

- Demonstration of a net solar-to-hydrogen PEC device conversion efficiency of 16% - the highest reported efficiency to date – and using a tandem PEC cell. The semiconductor materials used in this cell (gallium indium phosphide ($GaInP_2$) / gallium arsenide (GaAs), however, are still too costly for this to become an economically competitive technology in the near term. Successful alternative system designs using more abundant material combinations included amorphous silicon (a-Si) and tungsten trioxide (WO_3), the latter one in tandem with a dye-sensitised TiO_2 ("Graetzel") solar cell. Their demonstrated solar-to-hydrogen PEC device efficiency has been 7.8% and 4.5% respectively;
- Identification of new low-cost materials and advanced production methods (resulting in successful patent applications) have been identified. These include, among others, nano-structured, thin-film semiconductor photoelectrode materials based on iron oxide (Fe_2O_3), zinc oxide (ZnO), titanium dioxide (TiO_2), tungsten trioxide (WO_3) and various nitrides, above all InN and Sn_XN_Y;
- Establishment of equipment for fast-screening methods of electrochemical materials ("combinatorial chemistry") to study and identify optimum material combinations and to develop comprehensive material data libraries for electrochemical applications;
- Development of much improved Ru-based dyes for optimum light absorption in TiO_2 semiconductors, allowing to make better use of the solar spectrum toward the near-infrared radiation (up to 920 nm);
- Pre-commercial demonstration of 100mm x 100mm PEC laboratory cells based on WO_3 photoanodes and dye-sensitised TiO_2 solar cells, in collaboration with industry partners;
- Development and operation of a novel two-compartment PEC using a nanostructured AgCl layer as photocatalytic anode in combination with platinised silicon or $GaInP_2$ as counter electrode, demonstrating encouraging performance due to Br- and Au-sensitisation.
- Development of world-first powder photocatalysts for water splitting that can use not only the ultraviolet (UV) but also the blue part of the visible spectrum of sunlight;
- Analysis of the techno-economic potential of PEC devices, indicating that hydrogen production costs of the order of US$ 30 per GJ of hydrogen gas can be achieved with reliable PEC systems in a mid-term time horizon;

- Identification of promising economics when PEC hydrogen production is performed in conjunction with photodegradation of organic waste-water. Twofold efficiency gains seen with organic pollutants rather than water as reducing medium, combined with the cost/benefit of combining degradation of organic pollutants with hydrogen production, show great promise for commercial application;
- Definition of standards for measuring and reporting solar efficiencies. These standards are essential for making realistic comparisons between various photo-based systems for hydrogen production; and
- Participation of pioneering industry partners and venture capital groups confirm the great promise for sustainable commercial applications of PEC for solar water splitting.

In addition, non-scientific but important achievements for the collaborative Annex-14 task include:

- 6 expert meetings have been conducted, with a total of 120 PEC expert participants;
- 2 non-IEA-member (Israel, Mexico) and 7 non-Annex-member (Australia, France, Germany, the Netherlands, Norway, Puerto Rico, United Kingdom) country PEC experts participated as observers; and
- 5 researcher and/or specimen exchanges have been conducted among the four Annex-14 participation member countries.

4. Effectiveness toward Objectives

As Annex-14 development work progressed, material-based performance limitations have become more and more evident as being the prime research challenge for the advancement of PEC hydrogen production technologies. The main semiconductor materials that have been studied at the beginning of Annex-14 were neither effective nor stable enough in aqueous environments.

Therefore, searching for improved or alternative materials via combinatorial chemistry (fast screening of material options), doping for band engineering (gap and edge position), light absorption enhancement (particularly dyes), charge transfer optimisation (physical modelling and surface morphology adaptation), performance as well as stability improvements (catalysis and corrosion resistance), and thin-film deposition methodologies (CVD, spray pyrolysis, screen printing, etc.) have been at the forefront of R&D attention for Annex-14.

The need to focus R&D efforts on material challenges, precluded the experts of Annex-14 to work on component and system developments in accordance with the original program of work (PoW). As a direct consequence, system performance analyses comparing PEC devices with alternative solar hydrogen production routes had to be limited to the work where sufficient information, expert skills and funding was available, namely the techno-economic analysis of NREL's monolithic $GaInP_2$ / GaAs PEC device concept for concentrated sunlight.

Overall, the material studies component of Annex-14 has, from a scientific point of view, gone much beyond its original PoW while the system studies component was found to have reduced appropriateness at the given status of R&D knowhow, progress as well as achievements.

5. Effectiveness of National Participation

All of the four Annex-14 member countries, Japan, Sweden, Switzerland and the USA, participated well and in accordance with their planned commitment of national participation. In case of Sweden, however, contributions exceeded the contractual minimal commitment. In the US situation, the limited participation of the R&D group in Hawaii was compensated by exceptional participation of the three R&D groups in Colorado, Florida and California.

During its 4.5 years of operation, the Operating Agent has solicited progress reports from all of the four-member-country Annex-14 experts on a regular half-yearly basis in order to provide summary contributions for the Semi Annual Reports (SAR) as well as the Annual Reports (AR) of the Implementing Agreement.

In cases of foreseen non-participation possibilities at experts meetings, the Operating Agent ensured that the respective experts prepared and submitted progress reports for dissemination and discussion at the expert meetings.

The effectiveness of the four-member-country participation was further enhanced by numerous academic as well as industry observers that participated at the Annex-14 expert meetings upon invitation by the Operating Agent.

6. Participation by Industry

Focusing on the needs of fundamental as well as pre-competitive R&D, the scientific field of photoelectrolytic water-splitting does not yet provide a basis for industry involvement. Nonetheless, two companies have shown particular interest in the progress of Annex-14. These were Sustainable Technologies International (STI), an Australian technology development company focusing on the manufacture of TiO_2-based dye-sensitised solar cells, and Hydrogen Solar, a British start-up company planning to operate in the field of WO_3/TiO_2-based tandem-cells PEC cells.

7. Conclusion – Recommendation

Annex-14 is proud of having contributed toward a significant R&D focus as well as scientific progress worldwide in the area of photoelectrolysis of water. Dealing with a comparably young field of scientific endeavour (namely molecular material science and engineering) has brought about that the fundamental R&D conducted by the Annex-14 expert groups has not only found answers to some of the questions originally posed at the start of Annex-14, but has particularly uncovered a plethora of new scientific insights and challenges.

Given the encouraging achievements of Annex-14, and inspired by the significant rise in PEC R&D interest as well as activities that are being observed worldwide, it is recommended that a new 3-5 year follow-on PEC Annex be developed that aims to focus on solving the key material science challenges identified and pre-addressed during Annex-14 (refer to Subchapter 8).

8. Unresolved Scientific & Technical Issues

Although the experts working under Annex-14 have empirically identified and tested a number of new and improved photoelectrode material as well as system design options, it was found that major fundamental material science questions are in need of scientific investigation. These include above all:

- Optimum bandgap engineering solutions for semiconductors through anion doping;
- Sensitisation of semiconductors to extend light absorption toward the VIS light spectrum;
- Understanding of performance impact from bulk as well as surface material defects;
- Importance of nano-scale surface catalysis and associated kinetics;
- Corrosion resistance through thin-film surface passivation by metal-oxide thin-films;
- Fundamental studies of charge transfer mechanisms between semiconductor and metal-oxide interfaces; and
- Impact of thin-film preparation techniques on surface morphology of photoelectrodes.

Among the most important unresolved technical issues are:

- Thin-film deposition techniques (quality and performance control);
- Device design optimised for low-cost manufacture (monolithic devices, tandem systems, powder basins); and
- Gas handling, particularly gas separation with photocatalyst powder systems.

9. Information Dissemination Activities

The experts together with the Operating Agent of Annex-14 have focused their information dissemination efforts on three different activities. These were:

- Publishing of scientific papers in international material science and hydrogen energy expert journals;

- Presentations of Annex-14 work and achievements at international as well as national conferences and to government as well as community groups; and
- Ongoing reporting to the Executive Committee (ExCo) of the Hydrogen Implementing Agreement (HIA) through Semi-Annual and Annual Reports, including web-publishing of the Final Report of Annex-14.

10. Management Recommendations

Although there was a multitude of issues that have come up for improvement throughout the 4.5-year conduct of Annex-14, four dominant issues have been identified. These are:

- Leadership: The concept of subtask leadership has proven to be superfluous. Project management needs are all taking place effectively on a institute-by-institute basis while program guidance has been in the hands of the Operating Agent. It is recommended that the concept of subtask leadership be cancelled with fundamental R&D Annex programs;
- Travel Funding: Participation at expert meetings is most crucial but often impossible due to insufficient (or at times inexistent) budget allocation. It is recommended that the ExCo consider establishing a travel assistance program;
- US Travel Approvals: US Annex-14 experts experience significant bureaucratic hurdles to travel overseas. It is recommended that the ExCo initiates discussions with the DoE hydrogen program manager that (ideally) lead to a travel authorisation procedure that is managed by the ExCo member of the USA; and
- New Member Countries: Annex-14 has operated with a growing number of “permanent” observers from non-member countries. It is recommended that the ExCo takes a more proactive approach to expedite and secure new country membership applications.

11. Expert Meetings

Table-1 lists the six expert meetings that have been conducted during the Annex-14 program.

Table-1: List of expert meetings conducted as part of Annex-14.

Meeting	Date	Venue	Attendance
Kick-off meeting	7-9 October 1998	NREL, Golden, USA	9
1st expert meeting	14-15 March 2000	ANU, Canberra, Australia	7
2nd expert meeting	1-3 November 2000	EPFL, Lausanne, Switzerland	17
3rd expert meeting	10-12 September 2001	Angström Centre, Uppsala, Sweden	10
4th expert meeting	3-4 August 2002	Hokkaido University, Sapporo, Japan	11
5th expert meeting	27-28 April 2003	Accueil Ass. Ranleigh, Paris, France	21

12. Participating Experts

Japan, Sweden, Switzerland and the USA have been the official member country participants of Annex-14, which combined their respective R&D programs on photoelectrolysis of water.

The following research groups and experts have been active in Annex-14:

- **Japan**: The Photoreaction Control Research Center (PCRC) of the Japanese National Institute of Advanced Industrial Science and Technology (AIST) – Prof Hironori Arakawa and Dr Kazuhiro Sayama;
- **Sweden**: The University of Uppsala (UniU) – Prof Sten-Eric Lindquist and Dr Torbjoern Lindgren;
- **Switzerland**: The University of Geneva (UniG) – Prof Jan Augustynski, the University of Bern – Prof Gion Calzaferri and Dr Antonio Currao (UniB), and the Swiss Federal Institute of Technology (EPFL) in Lausanne – Prof Michael Graetzel and Dr mdKhaja Nazeeruddin; and
- **USA**: The National Renewable Energy Laboratories (NREL) – Dr John Turner, the Hawaii Natural Energy Institute (HNEI) – Dr Eric Miller, the Florida Solar Energy Centre (FSEC) – Dr Clovis Linkous, and the University of California (UCal) – Prof Eric Mcfarland and Dr Tom Jaramillo.

Toward the end of Annex-14, these about official member country participants have enjoyed a growing information exchange and/or part-collaboration with additional research groups that have secured funding to work in PEC water-splitting. Particularly since the second half of 2002, some of those non-Annex-14 and/or non-HIA member groups have started to attend Annex-14 expert meetings as observers on a regular basis. The key observer groups included:

- **Australia**: Sustainable Technologies International (STI);
- **France**: National Centre for Scientific Research (CNRS) and Atomic Energy Research Centre (CEA);
- **Netherlands**: Delft University of Technology (DUT) and Leiden Institute of Chemistry (LIC);
- **Mexico**: Energy Research Centre of the National University of Mexico (UNAM); and
- **United Kingdom**: Hydrogen Solar Company Ltd. (HSC).

13. Level of Efforts

Overall, the combined level of efforts invested by the nine participating research groups over the 4.5-year duration of Annex-14 amounted to an equivalent of about 80 – 85 “man-years”.

14. Outlook

Integrated PEC devices offer great potential for simplicity, thin-film-based mass production, application of environmentally benign and abundant materials, and therefore cost reduction compared to alternative solar-driven hydrogen production options. The materials science and engineering needs and long-term potential of PEC water-splitting cells are strongly related to the ones of fuel cells and photovoltaics, indicating that PEC systems have the capability of becoming a prime technology innovation building block of the future energy technology mix.

Although not yet achieved as part of Annex-14, the ultimate goal of stable PEC-based water-splitting technologies that operate with a sunlight-to-hydrogen conversion efficiency of 10% is in sight.