INDUSTRIAL DEVELOPMENT OF PHOTOELECTROCHEMICAL MODULES

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ABSTRACT

The project, which is part of the national Danish solar energy programme, aims at developing a production process for photoelectrochemical (PEC) devices for electricity or hydrogen production. The present paper presents the achievements during the first phase of the project.

INTRODUCTION

From fiscal year 2000, the Danish parliament specifically introduced R&D on photoelectrochemical (PEC) solar cells into the national budget. This recognition of the field was largely due to the successful initial work of the Danish Technological Institute. The Institute had in a short time reproduced a cell of similar standard to that achieved internationally (based upon the components suggested by Grätzel and colleagues [1,2]). Furthermore, they had initialised demonstration of a fabrication process suitable for industrial production with emphasis on encapsulation and sealing of the cells, which is considered as a key issue for the cell stability and lifetime. The parliament felt that the PEC technology was well adapted to the structure of the Danish manufacturing industry, which by necessity concentrates on excellence in a number of selected areas, rather than maintaining a "full range" of industrial products.

The presentation below first summarises the work carried out during the first year of government supported R&D, and further sketches some of the currently ongoing activities for the second year of the program.

1. Status of R&D effort directed at industrial production

The goal of the first year of the Danish effort was to acquire the skills to produce each component in a PEC cell. The production is based upon established techniques, but with consideration of the possibility of an early identification of the areas, in which improvements might be obtained, and as an overriding concern the need to identify techniques suitable for scaling up to a production line implementation.

A PEC cell captures solar radiation in a "sensitiser-coated" surface layer of a semiconductor, thereby exciting an electron, which is transferred to and transported across the semiconductor to an electric contact. The sensitiser is reconstituted by an electron from a counter-electrode, through a Redox reaction in an electrolyte present in the external space between the sensitized semiconductor and the counter contact material.

The starting point for fabrication of PEC cells or PEC modules is a set of two glass substrates, upon which the semiconductor electrode and the counter electrode, respectively, are built.

Before building the electrodes both substrates are provided with a thin but dense layer of SnO_2 serving as a surface conductor and as a chemical barrier protecting the underlying silver conductor lines from the aggressive electrolyte present inside the cell. The deposition of SnO_2 is in an industrial context a standard procedure used in already commercial products, with the coating deposited when the glass is being rolled out.

A nanoporous TiO_2 semiconductor electrode is deposited on one of the glass panes, using a CVD (chemical vapour deposition) assisted sol-gel technique (i.e. forming a solid network by reactions in a solution, leaving the solvent liquid within the network as an easily removed gel). The key issue in this process is to build a network of nanosized TiO_2 particles in-situ and at sufficient high speed. The developed CVD-assisted process is designed for high process throughput and process controllability. Furthermore, the process offers unique possibilities for building up layered structures, in which the size of the TiO_2 particles can be varied systematically as function of distance from the substrate. A structure consisting of a mixture of small particles (10 nm) and larger particles (200 nm) has been suggested to help scattered light paths in reaching the grain surfaces [3], but it probably has no effect on the ease of electron transport [10]. The purpose is to have as large an accessible collecting surface as possible (typically three orders of magnitude above the geometrical area), with the constraint that

transport in both semiconductor and in electrolyte should proceed without significant obstacles. The semiconductor properties may, if necessary, be controlled by doping.

In parallel to the processing of the semiconductor electrode, the counter electrode is manufactured on the second glass. The most viable route for depositing the catalyst (conventionally platinum - required for efficient transfer of an electron charge to the Redox cycle in the electrolyte) seems at present to be by spraying a platinum-containing precursor on the substrate and subsequently converting the spray layer to a platinum catalyst of desired structure by carefully controlled annealing.

The semiconductor and the counter electrode are now present on the two glass panes that will form the exterior of the finished cell. The next step is a partial sealing of the cell, where the four edges of the glass panes are sealed, but still leaving small openings in order to make the interior of the cell accessible for introducing the photoactive sensitiser and the electrolyte at a later stage. An inorganic seal developed specifically for this purpose is used. The semiconductor electrode, the catalyst and the edge sealing, all present in their conditions of formation, are at this stage annealed in a one-step process, which stabilise the entire structure both chemically and mechanically.

The next processing step is adsorption of the photoactive sensitiser on the TiO_2 surface, which itself has poor light absorption properties. The conventional, slow process of attaching the dye to the semiconductor grain surface by days of soaking is replaced by a method in which the sensitiser is pumped through the cells interior and the semiconductor is thereby subjected to a continuous flow of sensitiser. The adsorption of sensitiser in the cell, i.e. on the semiconductor surface, is monitored by a spectrophotometer.

When adsorption is completed, the cavity inside the cell is filled with a suitable electrolyte. Due to our use of hermetical seals, we can use the highly volatile mediator acetonitril. The remaining small openings, which were used for appllication of sensitiser and electrolyte, are now sealed and the cell is then ready for mounting electric connections.

Current module sizes (12 cells) are 0.18×0.25 m^2, which is a suitably large laboratory-scale size to explore fabrication processes without having to use apparatus (furnaces, etc.) capable of handling the ultimate window size cells. The structure of the cell components is verified by a number of techniques, including scanning electron microscopy, time-of-flight single-isotope

mass spectroscopy, atomic force microscope. Standardised efficiency measurements are performed using the Danish Technological Institute's solar test station equipment.

In the first phase of the project, dyes already identified as suitable for PEC cells [4,5] were synthesized from ruthenium chloride and locally synthesized ligands. Dyes with high absorption at the solar spectral frequencies are *cis*-[Ru^{II} (4,4'-dicarboxy acid-2,2'-bipyridin)$_2$ (NCS)$_2$] and [Ru^{II} (4'-phosphonate-2,2':6',2''-terpyridine) (4,4'-dimethyl-2,2'-bipyridine) (NCS)]. It was necessary to modify the literature prescriptions (expanding the suggestions in [6-8]), in order to obtain reasonable yields and sufficient purity. The manufacturing time has been reduced from days to hours. Further work on dyes is postponed till after the completion of theoretical studies aiming at optimising sensitiser properties. The ultrafast transfer (under 1 ns) of the dye electron excited by light to the semiconductor and the competing reactions will be discussed further below.

For the electrolyte, some possible solid semiconductor materials have been tested by various groups, but so far without obtaining very high overall efficiencies. Using a polysiloxane gel polymer network with plasticizing polyethyleneoxide chains, a cell efficiency of 3% has been reached [9]. The problem is in part due to the lack of total area contact between the dye and the counterelectrode material, which is precisely the reason that nearly all current systems use a fluid electrolyte capable of completing a redox cycle. One reasons for not being able to deposit a new semiconductor layer as a solid electrolyte is that the temperatures required for annealing or sintering (in order to get the material into cavities) is higher than the temperature around 360K, where the dye decomposes. While it is possible to deposit the TiO$_2$ semiconductor at lower temperatures, this reduces either surface area or conductivity. So far, we are using the same I^-/I_3^- Redox cycle in a solvent electrolyte as most other investigators. The recombination of a charge from the electrolyte to the vacancy in the sensitiser is a fairly slow process, that may determine the overall current [11,12].

Enhanced cycling techniques will be used to test the cell life time under relevant conditions.

2. Program outline for modelling and theoretical optimisation

Presently, only some of the process steps occurring in an illuminated PEC cell are well understood. Charge transport in the electrolyte is a conventional diffusion process, whereas charge propagation in the semiconductor is not. It has been reproduced in a fairly *ad hoc* random walk model [13], but still the experimental recombination data from the same study (follow-

ing photoexcitation by a short laser pulse) exclude simple diffusion [14] and probably also hopping models with tunnelling [13].

The excitation by solar radiation of the sensitiser, e.g. the ruthenium complexes mentioned, is believed to involve the absorption of a light quantum near the ruthenium centre, followed by the transfer of an electron to a π-orbital in the ligand [2]. The exact nature of the quantum transitions and states seem to have received little attention, and we are attempting to describe them by Hartree-Foch models (considering the motion of the last electron as taking place in a mean field produced by the other charged particles in the system), first for the sensitiser alone but subsequently taking into account the attachment to a surface (e.g. by the two oxygen atoms of the carboxylated bipyridyl ligand, coupling to the surface Ti-atoms) and the presence of electrolyte ions. Spectral analysis of the absorption and recombination dynamics has indicated the importance of localised trap states (e.g. states below the conduction band lower edge) in the semiconductor surface area [15], and space charges building up in the surface region (e.g. due to the influence of magnesium or lithium ions from the salts furnishing the iodide for the electrolyte Redox cycle [12]). Several studies have looked at the slower back transfer of the electron from the semiconductor to the dye, in the absence of the current trough the cell [16].

A photo-excited electron in the senzitiser is transferred to the semiconductor surface in competition with deexcitation, then moving through the semiconductor if not transferred back to the dye, and finally reaching the conductor if not recombined in the semiconductor. Correspondingly, the sensitiser hole is filled from the electrolyte, is moving through the electrolyte and finally filled by an electron from the counter conductor, in competition with processes upholding the charge transport.

The optimal choice of sentitizer is determined by location of its energy levels, notably the first excited level, which should be suitable for introduction of the electron into the semiconductor conduction band or lowered surface trap states. Further, the back transfer should be weak compared with the forward electron transfer, which should also out-compete deexcitation in the dye. On the electrolyte side, energetics should favour filling the electron hole at a reasonably fast rate. The ruthenium complexes are doing fairly well, with 70-80% incident light to injected electron efficiency in the frequency range of 450-750 nm, for the Ru-terpy complex, and somewhat less for the Ru-bipy complex. The best organic dye found so far is a modified coumarin-343 with an extra cyano carboxyl group broadening the frequency band of

absorption and facilitating adsorption to the semiconductor surface [17]. Its absorption spectrum matches that of the Ru-bipy complex, and the overall cell efficiency obtained is 5-6%.

Questions of cell durability include those of the stability of the sensitiser and of the corrosive nature of the electrolyte. There have been only few theoretical studies of stability, since the first assessment [18] of an early Grätzel cell [1], which finds serious instability problems of the ruthenium complex then proposed. Newer studies have been satisfied with apparent stability over periods of a few years, and there is a clear need for enhanced degradation studies.

DISCUSSION AND CONCLUSIONS

We use of a very result-oriented approach to exploit the break-troughs obtained over the last ten years in making solar cells based upon surface absorption of radiation (rather than conventional volume absorption in pn-junction semiconductors). This means that we work on several levels, from basic research to industrial production implementation, at the same time. We believe that the introduction of dye-sensitized solar cells has only a relatively short window of opportunity, in a period where conventional photovoltaic (PV) cell prices have (momentarily?) stopped declining while still being uncompetitive with other renewable power options (such as wind energy at favoured locations), except for certain niche markets. The feature that makes PEC cells interesting is the promise of low production costs, which again translates into finding the right materials and industrial schemes, rather than sophisticating the design details.

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