Chimia 57 (2003) 655–658

ISSN 0009–4293

Water Treatment Without Chemistry

Philippe Rychen*, Werner Haenni, and Laurent Pupunat

Abstract: Thin-film boron-doped diamond coatings (BDD/Si) on boron-doped silicon substrates by means of a large-scale hot-filament chemical vapor deposition (HF CVD) process have been developed in order to be used as an innovative and efficient electrode material, mainly to promote electrochemical water treatment applications without using chemicals. Electrochemical performance from anodic as well as cathodic points of view results from extremely high chemical and mechanical stabilities as well as the largest known electrochemical window. They correspond to the primary conditions for an electrode in order to facilitate water processing like disinfection and reduction of the chemical oxygen demand (COD). These electrodes have the production capacity of the strongest chemical oxidizing agents in water *i.e.* hydroxyl radicals. They may also be responsible for the electrochemical generation of other strong oxidants like chlorine, ozone, peroxodisulfates, peroxo-dicarbonates and hydrogen peroxide in many types of water, *i.e.* seawater, wastewater and fresh water, without the addition of any components.

Keywords: Boron-doped diamond electrodes · Disinfection · Electrolyser · Wastewater · Water treatment

Introduction

The development of new types of electrode materials for many electrochemical process applications, such as synthesis of inorganic and organic materials as well as galvanics – especially water treatment – remains a major challenge for scientists specialized in material engineering.

Electrode materials must meet the following parameters to enable water purification:
– adapted electrical conductivity
– chemical and electrochemical long-term stability
– electrically reversible (anode becoming cathode and reverse)
– no fouling
– good mechanical stability
– cost-effective production.

The long-term stability is one of the most significant conditions, above all when a periodic reversal polarity occurs. The use of electrode materials susceptible to corrosion leads to unneeded and sustained water contamination, whose elimination and/or passivation bring about supplementary costs for the replacement.

The field of electrochemistry had to wait until now for such equipment. It is in some way understandable that the industry has time after time lost interest in electrochemical processes. Those processes are also still considered as being harmful for environment and as lacking efficiency.

But this should now change with the electrode materials presented here – the boron-doped diamond electrodes.

Only in the last decade, some scientists have found out that electrically conductive diamond, boron-doped diamond, is an outstanding electrode material. The U/I diagram produced by cyclic voltametry displays an electrochemical window that could not be achieved before; the performance depends on purity and doping of diamond. Fig. 1 shows a cyclic voltammogram (CV) of a diamond electrode. Additionally, the performance of a conventional electrode made of platinum, a nitrogen- and boron-doped diamond electrode (NBDD)

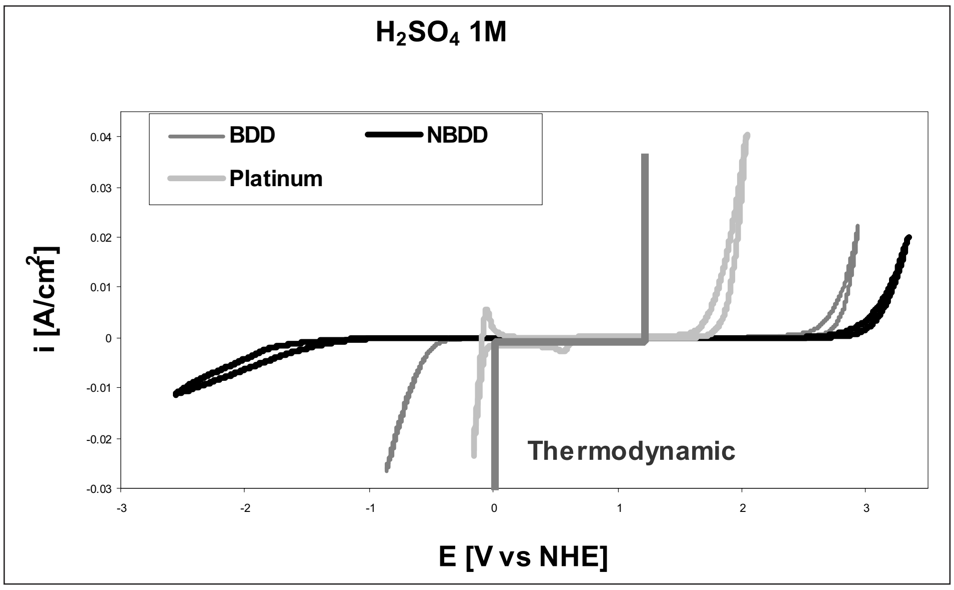

Fig. 1. Cyclic voltammogram of electrodes made from boron-doped diamonds (BDD), platinum, and nitrogen/boron-doped diamond

*Correspondence: P. Rychen
The Swiss Center for Electronics and Microtechnology Inc. (CSEM)
Jaquet-Droz 1
CH–2007 Neuchâtel
Tel.: +41 32 720 55 54
Fax: +41 32 720 57 10
E-Mail: philippe.rychen@csem.ch

CHIMIA 2003, 57, No. 10

as well as the thermodynamic area of water decomposition are presented to enable better comparison. We have to consider from now on that this new type of diamond electrode, compared with conventional electrodes, withstands considerably higher overloads and facilitates new or until now unknown electrochemical processes, which in fact could not be obtained or with only negligible results.

Results and Discussion

Electrode Manufacture

During the last 20 years, several processes have been developed for diamond production worldwide: using the gas phase, below atmospheric pressure, between 500 and 1000 °C – so-called CVD processes. Only one of these processes is suitable for extensive manufacture (0.3 to 0.6 m^2) of diamond films with thicknesses measured in micrometers and to which are mixed quantities of boron added separately or homogeneously. The pioneering work has been achieved by CSEM SA (Swiss Center for Electronics and Microtechnology AG, Neuchâtel) and FhG-IST (the Institute for Layer and Surface Technology of the Fraunhofer-Gesellschaft in Braunschweig, Germany). It involves the hot-filament chemical vapor deposition process, in which filaments are heated above 2000 °C in a gas reactor and arranged above the component to be coated. A gas mixture composed of hydrogen and methane is generated when pure diamond is being produced, and also for all other carbon forms (such as graphite and so on...). The temperature induced by the filaments heats up even the component being coated to between 750 and 900 °C.

The preferred substrate for the BDD-layer is diamond itself. For many understandable reasons, this shall however be considered separately. The best substrate for BDD-layers after diamond itself is silicon for many chemical and physical reasons.

The DiaCell® Concept

Silicon as a substrate for BDD/Si electrodes remains a real 'outsider' for industry applications, as no experiment has been done with this material. By taking into account this fact and the new and suitable BDD/Si electrode material, a robust, compact and modular electrochemical cell system, which is easy to handle has been developed, called the DiaCell® concept. It has proved its worth in laboratories as well as in the industry by use in pilot installations. Approximately 30 systems have already been produced and put in place. Further systems designed for higher flows and bigger electrodes will be designed and mounted.

The DiaCell® concept in Fig. 2 is based on the use of BDD/Si disk electrodes having a diameter of 100 mm and designed for pressures up to 6 bar. In that system, besides both electrically connected monopolar electrodes, a bipolar electrode has also been set-up. This construction facilitates the work with up to five compartments and four bipolar electrodes in one system. The system allows operations with the same stream up to 50 V/DC and to 200 A. This enables a current density of many mA/cm^2 up to 3 A/cm^2. Interelectrode distance can be set between 1 to 10 mm. The flows per compartment are approx. 250 l/h at 1 mm of interelectrode distance, *i.e.* flows of >1m^3/h can already be treated with a system containing five compartments.

As already explained, these DiaCell® concepts will be produced for laboratory tests but also for disinfection of typical swimming pool water.

The pilot plant has been designed for tests on a large and industrial scale with a system of five compartments (Fig. 3). It will be possible to turn on several DiaCell® systems simultaneously in parallel and/or in series. Modules can be built as well with separated compartments, membranes or diaphragms.

Examples of Water Treatment Applications

The DiaCell® concept was initially developed for water purification and disinfection in private swimming pools. Since then, it has proved to be suitable for many further water treatment applications, with the aim to provide solutions without adding chemicals.

During water electrolysis using BDD/Si electrodes in DiaCell® systems, further and more powerful disinfection agents besides the well-known chlorine technique, such as persulfate, percarbonate, ozone, and hydrogen peroxide are being generated directly from water or from its naturally occurring minerals. Thanks to scientific research at several places, it is known that hydroxyl radicals are generated at BDD/Si electrodes. Apart from fluorine, they provide the strongest oxidation process and help to maintain the above-mentioned disinfection or oxidation processes as well. Concentrations for individual disinfection methods depend on the specific water composition.

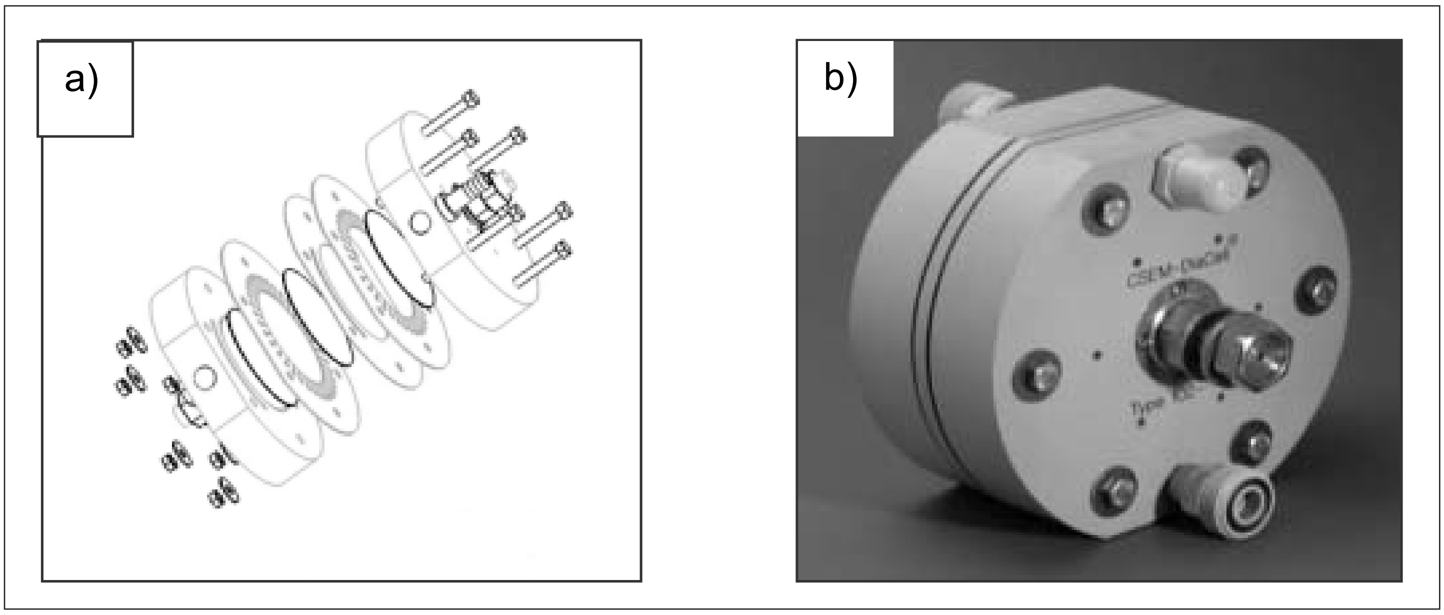

Fig. 2. The DiaCell® concept

CHIMIA 2003, 57, No. 10

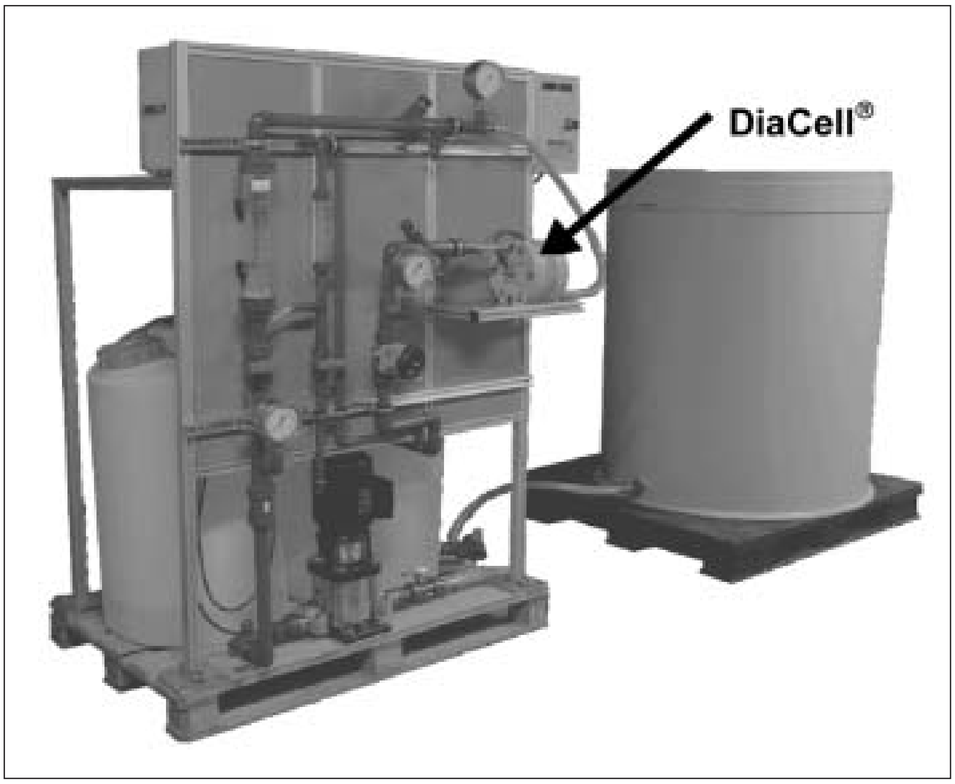

Fig. 3. Pilot plant for industrial water purification with a 1 m^3 tank

Disinfection of Swimming Pool, Sea- and Drinking Water

Widespread studies have been carried out by using those three water types in comparison to the traditional disinfection process with sodium hypochlorite solution. The tests involved different microorganisms including *Legionella pneumophila*, *H40* bacteria, *Adenovirus, E. Coli*, *vibrio fischerii* and *pyrocystis fusiformis* protozoan.

Those studies have demonstrated that all tested microorganisms, including algae, were radically and completely inactivated by electrochemically generated disinfectants with BDD/Si electrodes. Inactivation of *H40* bacteria is represented in Fig. 4.

It can be therefore assumed that the bacteria shown in Fig. 5, which are harmful species for superior microorganisms, cannot resist effectively in the presence of the BDD/Si electrodes.

Elimination of Organics in Industrial Waste

Thanks to the DiaCell® concept with BDD/Si electrodes, it could be demonstrated that industrial waste burdened with COD can be efficiently treated in order to achieve very low values. This guarantees the following biological step.

For example, sodium benzosulfonate, a typical biocide chemical, could be eliminated thanks to this process with 95 to 100% down to COD values of <100 ppm. With the electrochemical treatment of such a solution in the DiaCell® system at approx. 10 Ah/l, biodegradation could be achieved during laboratory tests at 25 °C compared to initially 0 g CO_2/l (by using an untreated solution) to 4 g CO_2/l. The biological degradability was determined by measurements of CO_2 contained in the solution.

The DiaCell® concept will start with any type of water using periodic electrode reversibility. The BDD/Si electrodes facilitate those electrochemical processes without any problem, in contrast to all types of electrodes known before. The polarity change is necessary, in order to avoid mineral ($CaCO_3$ deposits) or organic fouling at the electrode surface.

The electrochemical process using BDD/Si electrodes shows significant potential and provides new and chemical-free treatment solutions for the future water treatment market.

Conclusion

This new concept for water treatment with the DiaCell® technology represents a genuine potential to become a new option for realizing strong and robust disinfection of microorganisms in drinking water, ballast water or even in wastewater treatment systems. The major advantage is the long-term sustained action of highly oxidizing agent generation due to the very large anodic overvoltage of BDD/Si electrodes.

The disinfectants produced with the DiaCell® are two to four times stronger

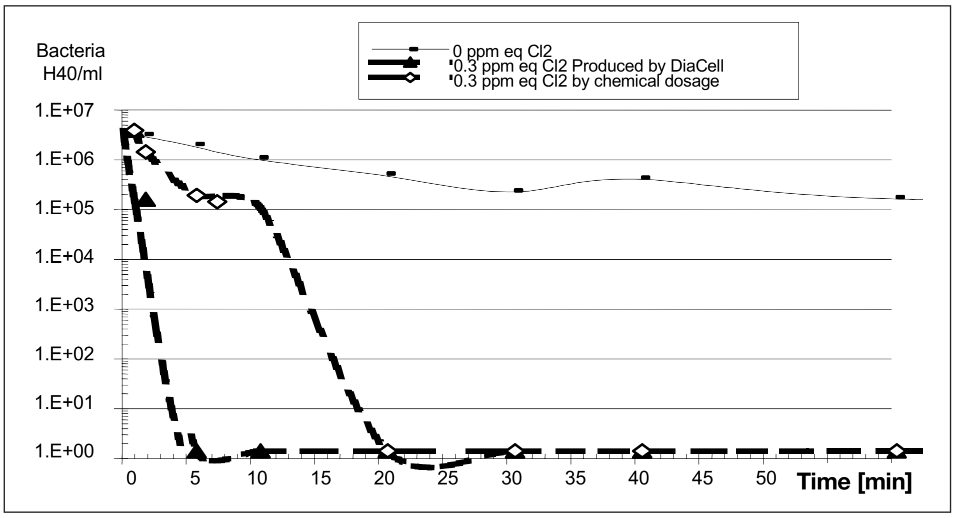

Fig. 4. Inactivation of *H40* bacteria (concomitant of adenovirus) in seawater with the DiaCell® concept and compared to the traditional method using sodium hypochlorite solution

CHIMIA 2003, *57*, No. 10

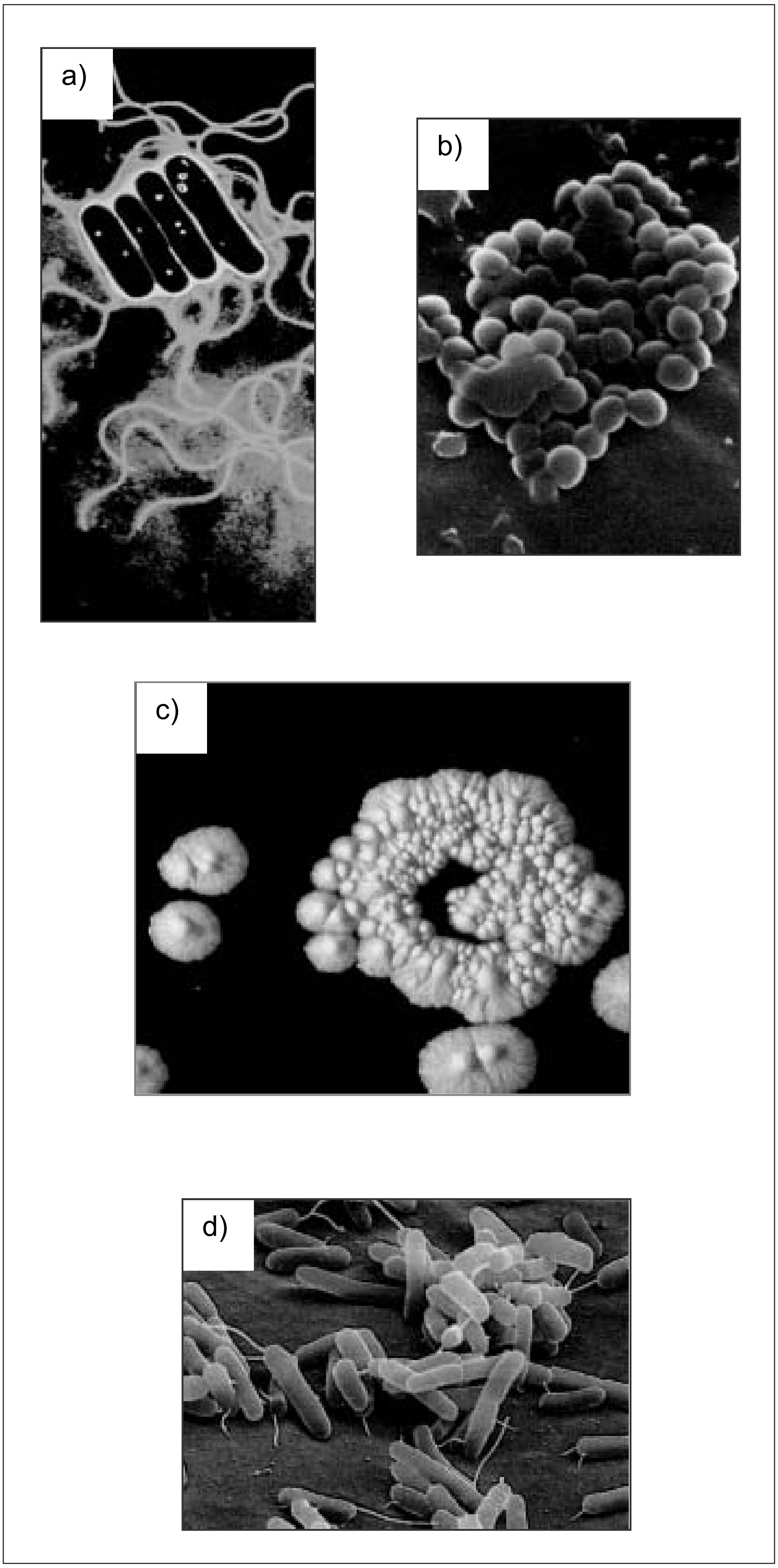

Fig. 5. Examples of typically strong resistant microorganisms

than chlorine. This technique is also able to prevent the regrowth of microorganisms in comparison to other typical water disinfection processes like UV-treatment.

The DiaCell® is the first electrolyser concept designed for BDD/Si electrodes, which shows a potential for different water treatment applications beside disinfection, mainly the COD destruction applications for industrial wastewater treatment. The next generation of Diacell® will be designed for larger electrode surfaces (factor 4 to 10) in order to be applied to more significant water flowrates.

Received: July 25, 2003

a) P. Rychen, L. Pupunat, W. Haenni, E. Santoli, 'Water Treatment Applications with BDD-Electrodes and the DiaCell® Concept', *New Diamond and Frontier Carbon Technology* **2003**, *13*, 109–117.

b) W. Haenni, J. Gobet, A. Perret, L. Pupunat, P. Rychen, C. Comninellis, B. Correa, *New Diamond and Frontier Carbon Technology* **2002**, *12*, 83–88.

c) S. Ferro, A. de Battisti, I. Duo, C. Comninellis, W. Haenni, A. Perret, *J. Electrochem. Soc.* **2000**, *147*, 2614.

d) L. Pupunat, P. Rychen, M.A. Fontecha-Camara, W. Haenni, B. Klaus, P. Rossi, Proceedings First International Conference on Ballast Water Management, Singapore, Nov. **2001**.