# Monday Morning, October 31, 2011

Marine Biofouling Focus Topic Room: 105 - Session MB-MoM

### **Interfacial Aspects of Marine Biofouling**

Moderator: D. Barlow, Naval Research Laboratory

### 8:20am MB-MoM1 Fouling in the Face of a "Little" Surface Roughness, R. Lamb, A. Wu, K. Cho, H. Zhang, The University of Melbourne, Australia INVITED

Nano-engineered superhydrophobic surfaces have been investigated for potential fouling resistance properties. Integrating hydrophobic materials with nanoscale roughness generates surfaces with superhydrophobicity that have water contact angles ( $\theta$ ) in excess of 160° and low hysteresis (< 10°).

Small angle x-ray scattering (SAXS) was used to investigate the presence of air incursions at immersed superhydrophobic interfaces with varying nano/microscale architecture. This technique, sensitive to local changes in electron density, looks at the nanoscale wetting of the rough interface.

Three superhydrophobic coatings differing in their chemical compositions and architecture were analyzed using SAXS and tested against major fouling species (*Amphora sp., Ulva rigida, Polysiphonia sphaerocarpa, Bugula neritina, Amphibalanus amphitrite*) in settlement assays.

Varying extents of attachment-inhibiting properties were observed across the tested coatings and appeared to correlate with the resistance to nanowetting rather than macroscopic contact angle measurements.

9:00am MB-MoM3 Chemistry Depending Surface Conditioning and its Implication for Colonization by Microorganisms, I. Thomé, Karlsruhe Inst. of Tech. (KIT), Germany, M.E. Pettitt, University of Birmingham, UK, S. Kirchen, T. Schwarz, S. Heissler, Karlsruhe Inst. of Tech. (KIT), Germany, M.E. Callow, J.A. Callow, Univ. of Birmingham, UK, G. Swain, Florida Inst. of Tech., M. Grunze, A. Rosenhahn, Karlsruhe Inst. of Tech. (KIT), Univ. of Heidelberg, Germany

Biofouling is a ubiquitously occurring phenomenon in tidal zones worldwide [1]. To prevent unwanted effects caused by biofouling, suitable non-toxic coatings for these environments are required. Changing the surface chemistry and the composition of a coating changes not only its properties but also the formation and composition of a conditioning layer. We use self-assembled monolayers (SAMs) on gold as highly controlled surface chemistries which allow to fine tune the physicochemical surface properties. In order to correlate colonization with surface conditioning, we varied the surface chemistry and thus their wetting properties. In agreement with previous work, chemical termination of the surface affects not only the settlement kinetics of spores of the macrofouler Ulva linza [2] but also the settlement of other species. As different SAMs have different affinity towards macromolecules, settlement is controlled by both, surface chemistry itself and an adsorbed conditioning layer. To disentangle both effects, formation of conditioning layers depending on the surface chemistry was investigated in greater detail by spectral ellipsometry and IRRAS. Organism settlement is significantly changed if pristine chemistries are compared to conditioned surfaces.

[1] M.E. Callow, J.A. Callow, J.D. Pickett-Heaps, R. Wetherbee, "Primary Adhesion of Enteromorpha (Chlorophyta, Ulvales) Propagules: Quantitative Settlement Studies and Video Microscopy", *J. Phycol.*, **1997**, *33*, 938.

[2] M. E. Callow, J. A. Callow, L. K. Ista, S. E. Coleman, A. C. Nolasco, G. P. López, "Use of self-assembled monolayers of different wettabilities to study surface selection and primary adhesion processes of green algal (*Enteromorpha*) zoospores", *Appl. Environ. Microbiol.*, **2000**, *66*, (8), 3249-3254.

#### 9:40am MB-MoM5 Probing Molecular Details of Marine Bioadhesion with In Situ Infrared Spectroscopy, A.J. McQuillan, University of Otago, Dunedin, New Zealand INVITED

The critical step which triggers biofouling at interfaces is the initial adhesion of an invading species to a solid substrate. Of less importance in what occurs thereafter is growth of the species under the infuence of nutrients and with the protection of its more sheltered environment. Understanding the factors determining the propensity of species to adhere to substrates is the key to developing new strategies aiming to more effectively inhibit the development of biofouling in many contexts.

Much of the thinking about biofilm formation and the adhesion of biological species to surfaces has been extrapolated from macroscopic observations about the aggregation of colloids. This has been largely based on the interplay between attractive dispersion forces and repulsive electrostatic forces and has given rise to adhesion descriptions in terms of reversible and irreversible stages. A major advance has been the use of in situ atomic force microscopy (AFM) to measure forces during adhesion of microbes to substrates and evaluate their environmental influences. Nevertheless, this approach is unable to provide in situ molecular details of the chemical components which are suspected to play major roles in adhesion processes.

Vibrational spectroscopy is powerful to reveal the identity and environmental details of molecules in wet interface environments. Vibrational sum frequency spectroscopy and infrared spectroscopy are increasingly thus employed. However, attenuated total reflection infrared (ATR-IR) spectroscopy has the advantages of relative simplicity and greater general familiarity in spite of its use for wet surface situations having only recently been recognised. The ATR-IR approach employs total internal reflection at a high index refraction crystal such as ZnSe or diamond resulting in an evanescent wave sampling a few micrometers of material.

In this talk I will outline the principles of the ATR-IR method and how we have adapted them for studies of initial settling of live marine organisms settling onto surfaces under controlled temperature and environment conditions. Observations from recently published work on the settling of Perna canalicula mussel larvae and Undaria pinnatifida kelp spores will be presented and prospects for breakthrough studies of the settling and propagation of the feshwater diatom Didymosphenia geminata, invasive to New Zealand, will also be discussed.

10:40am MB-MoM8 Relationships between Cement Production Cycles and Adhesive Strength of the Barnacle Balanus Amphitrite, D.K. Burden, D.E. Barlow, U.S. Naval Research Laboratory, B. Orihuela, D. Rittschof, Duke University Marine Laboratory, K.J. Wahl, U.S. Naval Research Laboratory

Marine organisms attach themselves to a wide variety of submerged surfaces. The barnacle is one of the most pervasive and persistent species to do so, securing itself by forming a thin film of permanent proteinaceous adhesive. For hard-shelled acorn barnacles like Balanus amphitrite, this process involves the recurring sequential release of two major secretions at the adhesive interface. We show that as the barnacle grows laterally, one of these cement precursor solutions, CPS1, is released on a fairly continuous basis, while the other, CPS2, is released cyclically. By utilizing the differences in secretion patterns, we have begun to deconvolve the contributions of these cement precursors to adhesion. Barnacles were resettled on CaF2 substrates and release of the components at the interfaces was distinguished by optical and fluorescence microscopy. Shear detachment measurements of resettled barnacles showed that the release of CPS2 into the interface corresponded with a roughly twofold increase in adhesion versus CPS1 alone. AFM and FTIR also showed distinct differences in morphology, protein conformation, and chemical functionality for the CPS mixture versus CPS1. Possible ways in which the two components contribute to barnacle adhesion will be discussed based on these results.

#### 11:00am MB-MoM9 Micro to Nanostructured Stimuli-Responsive Surfaces for Study and Control of Bioadhesion, G.P. Lopez, Duke University

This contribution will present recent results on the development and study of bioadhesion on stimuli responsive surfaces that are patterned on lateral length scales of the order of 10 microns and below. These length scales are commensurate with the sizes of the smallest creatures known to be problematic in marine biofouling. Model stimuli responsive surfaces include patterned polymer brushes and model marine organisms include marine bacteria grown in culture. Our previous studies have demonstrated that stimuli responsive materials can be used to control the adhesion of model marine organisms and this presentation will provide our latest advancements in this line of study, as regards to both molecular and cellular biointerfacial phenomena. Methods for preparing nanopatterns of stimuli responsive polymer brushes over areal scales necessary for biofouling studies will be presented, along with characterization of their structure and dynamic behavior.

11:20am MB-MoM10 Surface Topographic Features to Control Biofouling, L. Xiao, University of Heidelberg, Germany, M. Röhrig, Karlsruhe Institute of Technology, Germany, S.E. Thompson, M.E. Callow, J.A. Callow, University of Birmingham, UK, A. Rosenhahn, M. Grunze, University of Heidelberg, Germany

Marine biofouling is the undesirable accumulation of microorganisms, plants and animals on artificial surfaces immersed in the sea [1]. The increased hydrodynamic drag caused by fouling leads to higher operating costs of vessels. Studying the interaction between marine organisms and surfaces enhances the development of environmentally compatible approaches to control fouling [2]. Surface microtopography has been found to influence the settlement of cells and larvae [3]. We have studied the influence of surface topographic features on the biofouling process. Honeycomb gradient structures, inspired by the pattern found on the skin of the pilot whale [4], were obtained by a hot embossing process, and the effect on the density of spores of the green alga *Ulva* that attached in laboratory assays was quantified. Spore settlement density was higher on the microstructured gradients than the smooth background. The highest density of spores was found when the size of the microstructures was similar to or larger than the size of a spore. With decreasing size of the honeycombs, spore settlement decreased to a level similar to that on the smooth background. In line with the results from the Brennan group [5], spore settlement correlated with Wenzel roughness.

[1] D. M. Yebra, S. Kiil, K. Dam-Johansen, "Antifouling technology – past, present and future steps towards efficient and environmentally friendly antifouling coatings", *Progress in Organic Coatings*, **2004**, *50*, 75-104.

[2] M. E. Callow, J. A. Callow, "Marine biofouling: a sticky problem", *Biologist*, **2002**, *49*, (1), 1-5.

[3] A. J. Scardino, R. de Nys, "Mini review: Biomimetic models and bioinspired surfaces for fouling control", *Biofouling*, **2011**, *27*, (1), 73-86.

[4] X. Cao, M. E. Pettitt, F. Wode, M. P. Arpa Sancet, J. Fu, J. Ji, M. E. Callow, J. A. Callow, A. Rosenhahn, M. Grunze, "Interaction of zoospores of the green alga *Ulva* with bioinspired micro- and nanostructured surfaces prepared by polyelectrolyte layer-by-layer self-assembly", *Adv. Funct. Mater.*, **2010**, *20*, 1984–1993.

[5] M. L. Carman, T. G. Estes, A. W. Feinberg, J. F. Schumacher, W. Wilkerson, L. H. Wilson, M. E. Callow, J. A. Callow, A. B. Brennan, "Engineered antifouling microtopographies – correlating wettability with cell attachment", *Biofouling*, **2006**, *22*, (1-2), 11–21.

11:40am **MB-MoM11 Biofouling: It's a Rough Business**, *A. Wu, R. Lamb, A. McDonald*, The University of Melbourne, Australia

The effect of minute changes in nanoengineered superhydrophobic surfaces on the attachment behaviour of several fouling species (*Amphora sp., Ulva rigida, Bugula neritina*) was investigated.

Superhydrophobic surfaces were fabricated from latex-templated silica solgels<sup>1</sup>. Nanoscale features of the surfaces were varied using two building blocks; silica nanoparticles ranging from 7 – 40 nm and PMMA templating latex ranging from 400 – 800 nm. The combination of these building blocks affords various roughness changes at the nanoscale. In maintaing surface chemistry identical, all fabricated surfaces exhibited superhydrophobic characteristics.

Attachment assays of each surface were conducted and a large variation in attachment-inhibition behaviour was observed. Correlating this behaviour against measured AFM roughness suggests that an intricate relationship exists between surface roughness and attachment behaviour. Data indicate that surface fabricated using small nanoparticles (7 nm) coupled with large templating latexes and high RMS roughness (> 130 nm) exhibited significant attachment inhibiting behaviour. This set of criteria also conforms to the definition of a fractal surface, where self-similarity is present different length scales.

Coupled with previous work<sup>2</sup> that linked pseudo-fractal dimension with nanowetting, this work strongly suggests that resistance to nanowetting has a key influence on attachment of marine organisms.

1 Cho, K. L., Wu, A. H. F., Lamb, R. N. & Liaw, I. I. The Journal of Physical Chemistry C 114, 11228-11233, (2010).

2 Zhang, H., Lamb, R. N. & Cookson, D. J. Applied Physics Letters 91, 254106, (2007).

# Monday Afternoon, October 31, 2011

Marine Biofouling Focus Topic Room: 105 - Session MB+BI+PS-MoA

### **Marine Antifouling Coatings**

**Moderator:** A. Rosenhahn, Karlsruhe Institute of Technology, Germany

2:00pm MB+BI+PS-MoA1 Advances in Sustainable Technologies for the Prevention of Marine Biofouling, *R. Deshmukh*, University of Texas at Arlington, *P. Sheth*, University of North Texas Health Science Center, *R.B. Timmons*, University of Texas at Arlington, *J.A. Schetz*, University of North Texas Health Science Center INVITED

The cost associated with preventing the attachment of marine organisms to underwater surfaces (biofouling) is billions of dollars annually impacting numerous sectors including shipping, aquaculture, offshore drilling, and offshore tidal and wind power. Invariably the most effective biofouling control methods are ones that are biocidal in nature whereby a coating is impregnated with a toxin that leaches out over time. However, persistence and bioaccumulation of heavy metal-based and organic biocides, creates environmental and health problems that have resulted in their regulation. Vigorous hull cleaning, aimed at periodically removing biofouling organisms, disperses fine biocide-impregnated coating particles and this significantly increases biocide persistence in sediments where they are ingested by a variety of marine organisms and bioaccumulate.

Coatings that peel off under conditions of high shear, so called foul-release coatings, are another approach but such coatings are easily damaged, not amenable to grooming and ineffective against microfouling. Further, the most effective foul-release coatings are silicon-based and it is becoming increasing apparent that leaching of toxic silicon oils from the coating matrix plays a role in their superior antifouling performance. Other approaches have been to develop durable coatings with little antifouling activity but that can withstand repeated intense grooming. One of our long term objectives is to identify coating materials with surface properties discouraging the settlement of biofouling organisms but also durable enough to withstand cleaning.

Here we report on the discovery of a transparent, conformal, pin-hole free, and plasma-polymerizable polymer coating made from an inexpensive monomer material that drastically reduces (>90%) algae (*Ulva*) sporeling settlement and biomass accumulation without any observable toxicity towards *Ulva* or a non-target brine shrimp species (*Artemia*). Further the unpolymerized monomer has no antifouling effect indicating that potential leaching of monomer from coated surfaces does not account for the observed antifouling activity. Rather the antifouling effect is believed to rely on the presence of a specific chemical moiety because chemical modification of that moiety abolishes antifouling activity. Testing of other marine antifouling mussels (*Ischadium*) suggests that the antifouling properties of the polymer surface are selective for algae. Potential unique applications for this technology include the coating of algae bioreactor walls or light fixtures allowing for maximal illumination and easy cleaning.

## 3:00pm **MB+BI+PS-MoA4 Development of a Comparative Protocol for Anti-Fouling Surfaces Based on Polymer Brushes**, *A. Serrano*, *S. Zürcher, S. Tosatti*, SuSoS AG, Switzerland, *N.D. Spencer*, ETH Zurich, Switzerland

Marine surfaces are known to accumulate fouling material through the starting point of adhesion and settlement of proteins and cells. This effect can be manipulated through the modification and control of the substrate properties via surface functionalization. This approach has led to successful anti-fouling coatings based on biocidal agents containing copper or zinc compounds<sup>[1,2]</sup>. The environmental toxicity of these latter materials, however, has increased the demand for less adverse coatings. The use of ultra-thin films consisting of polymer brushes has been considered a promising alternative and many studies have been published in this field<sup>[3,4]</sup>. None, however, has focused on developing a protocol that allows a reliable comparison between the efficiency of different well-known anti-fouling polymers. This is one of the aims of this work and has been achieved by using a common, azide-terminated monolayer to which different nonfouling polymers, such as PEG, PEOXA, PVP and PVA, have been covalently bound. The different materials were compared by characterizing the structure-property relationship of the formed polymeric brushes. Also investigated was the role of the solvent used in the anti-fouling polymer solution as a key element to better control the surface homogeneity. A thorough analysis of the influence of this parameter on the conformation of the final polymer brush was based on ellipsometry, XPS and imaging ToF-

SIMS. Finally, the anti-fouling surfaces were subjected to a comparative biological study by exposure to complex proteins solution and *Ulva* zoospores, in order to validate the developed protocol.

References:

<sup>[1]</sup> Magin, C.M.; Cooper, S.P.; Brennan, A.B., *Materials Today*, **2010**, *13*, 36-44.

<sup>[2]</sup> Chambers, L.D.; Stokes, K.R.; Walsh, F.C.; Wood, R.J.K., *Surface & Coatings Technology*, **2006**, *201*, 3642-3652.

<sup>[3]</sup> Banerjee, I.; Pangule, R.C.; Kane, R.S., *Advanced Materials*, **2011**, *23*, 690-718.

<sup>[4]</sup> Krishnan, S.; Weinman, C.J.; Ober, C.K.; Journal of Materials Chemistry, **2008**, *18*, 3405-3413.

3:40pm MB+BI+PS-MoA6 Surface Modification of Polymers via Self-Stratification: Decoupling of Bulk and Surface Properties, D.C. Webster, North Dakota State University INVITED Since materials interact with their surroundings via their surfaces, controlling the surface properties of a material are of critical importance. For materials to be used to mitigate biofouling, having the correct surface properties means the difference between a useful material and one that is unsuitable for the application. In many cases, the material properties of compositions which yield useful surface properties are not suitable for the bulk properties of the material. Thus, being able to decouple the surface and bulk properties is of interest in many areas.

Combining polydimethysiloxane (PDMS) with other polymer systems generally results in materials covered with PDMS due to its low surface energy and incompatibility with other polymers. However, if the PDMS is not chemically bound into the system, it can be easily removed from the surface. Thus, forming a copolymer of the PDMS with the other polymer is required for a durable system. Since polyurethanes are known as tough polymers due to extensive internal hydrogen bonding, combining PDMS with a polyurethane could lead to a material which is tough, but has a low surface energy surface provided by the PDMS. Thus, we have found that incorporating a reactive PDMS into a crosslinked polyurethane system can result in a material which has a low surface energy which is stable when immersed in water. High throughput screening has been used to aid in the identification and optimization of PDMS molecular weight, composition of end groups, and the amount of PDMS in the coating. A unique coating was also identified having discrete domains of PDMS on the surface. Coatings having good fouling-release properties have been prepared and tested in ocean immersion testing.

4:20pm **MB+BI+PS-MoA8** Antifouling Behavior on the Surface of **Polyelectrolyte Brushes in Water**, *M. Kobayashi*, *M. Terada*, Jst, Erato, Japan, *A. Takahara*, IMCE, Kyushu University, Japan

Nature utilizes super-hydrophilic surfaces under wetted state by water to achieve oleophobicity and self-cleaning behavior. For example, fish can maintain a clean body surface by surrounding a thin layer of mucus containing calcium phosphate and protein, which protects oil attachment, marine fouling, and adhesion of marine organisms. In this study, highdensity hydrophilic polymer brushes were prepared on Si-wafer by surfaceinitiated controlled radical polymerization of methacrylate monomers with ionic functional groups.[1] For example, poly(3-sulfopropyl methacrylate potassium (PSPMK) and poly{2-(methacryloyloxy)ethyl salt) phosphorylcholine} (PMPC) brushes with 50 - 100 nm thickness repelled both of air bubble and hexadecane droplet in water.[2] Even when the silicone oil was spread on the polyelectrolyte brush surfaces in air atmosphere, once the oil-sitting brush substrates were immersed in water, the oil quickly rolled up and detached from the brush surfaces due to the low adhesion force between the brush and oil caused by excellent affinity of polyelectrolyte brushes to water. Similar oil detachment behavior was observed on the hydrophilic poly(sodium methacrylic acid) (PMANa) and poly[3-{dimethyl(2'-methacryloyloxyethyl)ammonio} propanesulfonate (PMAPS) brushes,[3] whereas the oil still remained attached on the hydrophobic poly(2-perfluorooctylehtyl acrylate) (PFA-C8) brush even though the PFA-C8 brush shows relatively oleophobic property under air atmosphere. These hydrophilic brush surfaces would contribute to the excellent self-cleaning, antifogging, and antifouling properties without any surfactants

[1] M. Kobayashi, M. Terada, Y. Terayama, M. Kikuchi, A. Takahara, Macromolcules 2010, 43 8409.

[2] M. Kobayashi, Y. Terayama, N. Hosaka, M. Kaido, A. Suzuki, N. Yamada, N. Torikai, K. Ishihara, A. Takahara, Soft Matter 2007, 3, 740.

[3] Y. Terayama, M. Kikuchi, M. Kobayashi, A. Takahara, Macromolecules 2011, 44, 104.

4:40pm **MB+BI+PS-MoA9** Non-fouling Polymer Chemical Gradients for the Investigation of Marine Bioadhesion, *O. Sterner*, ETH Zurich, Switzerland, *S. Zürcher*, SuSoS AG and ETH Zurch, Switzerland, *S. Tosatti*, SuSoS AG and ETH Zurich, Switzerland, *N.D. Spencer*, ETH Zurich, Switzerland

The accumulation of marine organisms on submerged man-made structures (referred to as marine biofouling) has great economical and environmental impact [1]. Numerous strategies to prevent or lower the extent of marine biofouling have been developed, ranging from biocidal coatings to coatings that either prevent adhesion, lower the strength of adhesion or combinations thereof [2-4]. Surface gradients offer a high-throughput approach to investigate the potency of such coatings, and have the additional advantage of reducing the error in experiments by replacing a set of single samples, including positive and negative controls, with a single substrate [5]. In this project, polymeric ultrathin coatings have been prepared using a versatile surface functionalization system based on a self-assembled monolayer of poly(allyl amine) grafted with photo sensitive perfluorophenyl azide functional groups. Gradients have been prepared using a straightforward approach to control the extent of azide to nitrene conversion over the surface, forming a polymer density gradient. Gradients of poly(ethylene glycol), poly(2-ethoxy-2-oxazoline) and poly(vinyl pyrrolidone) have been prepared and investigated for non-fouling action against zoospores from green macrofouling algae Ulva and two strains of marine bacteria. The gradients reveal a drastic reduction in bacterial adhesion at low polymer densities for all polymers investigated. Gradients have been characterised with variable angle spectroscopic ellipsometry (VASE) and the properties of the polymer coatings have been evaluated with time-of-flight secondary ion mass spectroscopy (TOF-SIMS) and XPS.

#### References:

1. Schultz, M.P., Biofouling, 2007. (5): p. 331-341.

- 2. Chambers, L.D., et al., Surf Coat Tech, 2006. (6): p. 3642-3652.
- 3. Grozea, C.M. and G.C. Walker, Soft Matter, 2009. (21): p. 4088-4100.

4. Krishnan, S., C.J. Weinman, and C.K. Ober, J Mater Chem, 2008. (29): p. 3405-3413.

5. Morgenthaler, S., C. Zink, and N.D. Spencer, Soft Matter, 2008. (3): p. 419-434.

#### 5:00pm MB+BI+PS-MoA10 Development of Poly(silyl urethanes) with Tethered Quaternary Ammonium Biocides as Antifouling Marine Coatings, P.N. Coneski, N.K. Weise, J.H. Wynne, Naval Research Laboratory

Due to the significant economic burden posed by high operational and maintenance costs of biofouled ships, the design of environmentally benign, antifouling marine coatings has been a significant interest for many researchers since the ban on traditional coatings was enacted. Current approaches for developing new marine coating materials have primarily focused on the preparation of low surface energy materials, such as modified polydimethylsiloxane (PDMS) and fluorinated polymers. These materials have shown great promise for reducing the adhesion strength of various fouling organisms, thus allowing hydrodynamic forces to release the foulants as the ship moves through water. Unfortunately, no existing material has been shown to eliminate adhesion of all of the numerous different fouling organisms, including zoospores, microalgae and diatomaceous species. As such, the development of marine coatings with multiple mechanisms of fouling prevention may be an important avenue of antifouling materials research. Poly(silyl urethanes) coatings have been developed via the reaction of various quaternary ammonium modified orthosilicates with polyisocyantes. Material properties including glass transition temperature, surface energy, and thermal stability have been investigated as a function of orthosilicate and polyisocyanate composition as well the inclusion or omission of low surface energy soft segments. The low surface energy of these materials should provide excellent fouling release properties, as has been seen with other PDMS-like materials, while the inclusion of bound quaternary ammonium biocides should further reduce the adhesion and propagation of fouling organisms at the material interface. Finally, the hydrolysable silvl ether crosslinking may prove to enhance the antifouling capabilities of these materials by allowing any fouled portions of the coating to slough away over time, generating a new active biocidal interface.

5:20pm MB+BI+PS-MoA11 A Preliminary Study on Porous Pt-TiO<sub>2</sub>/Ti Electrodes with Electrochemically Microbubble-Induced Superhydrophobic Surfaces for Drag Reduction and Antifouling, *K.R. Wu*, *C.H. Hung, C.W. Yeh, J.C. Sun, J.K. Wu*, National Kaohsiung Marine University, Taiwan, Republic of China

We investigate a novel device that features a reduction in frictional resistance and antifouling hull surface of seagoing ships which are activated electrochemically by a series of porous Pt-TiO2/Ti electrodes. This device includes of a series of anodic and cathodic porous Pt-TiO /Ti electrodes insulatedly mounted on the hull surfaces of which are electrically connected to a direct current (DC) power supply. The above-mentioned porous Pt-TiO<sub>2</sub>/Ti electrodes are fabricated by two steps; porous TiO<sub>2</sub>/Ti plates are firstly prepared on pure titanium plates via a micro-arc oxidation technique and Pt nanoparticles are thereafter deposited on the porous TiO2/Ti samples using magnetron sputtering. The DC power supply provides an adequate DC bias to the Pt-TiO2/Ti electrodes where hydrogen and oxygen microbubbles are electrochemically nucleated and formed herein in seawater. As a result, the microbubble-induced superhydrophobic surfaces are created and the reduction in frictional resistance and antifouling hull surface are obtained. Our preliminary tests reveal that no attachment organisms are found on the Pt-TiO2/Ti electrodes after 15 days of field seawater tests at an applied potential of 1.2 V and an energy consumed rate of about 4 W/m<sup>2</sup>. On the other hand, organisms, mainly Crassostrea gigas and barnacles, attached and grew on the Pt-TiO2/Ti electrode that was not applied a DC potential. That is to say that attachment of organisms can be prevented. Furthermore, the Pt-TiO2/Ti electrodes yields a gas production rate of 800 cm<sup>3</sup>/min m<sup>2</sup> by electrolysis of seawater at an energy consumed rate of about 18 W/m<sup>2</sup>. Hence, the microbubble-induced superhydrophobic surfaces can be realized with this gas production rate for drag reduction of the ship hull.

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