

Electrical characterization of molecular films on silicon and of thin-film devices

Professor Hans Coster

Director Biophysics and Bioengineering, School of Chemical and Biomolecular Engineering, University of Sydney and Chief Scientist, INPHAZE Pty Ltd, Sydney, Australia

Abstract

Detailed characterization of the thin films, depletion layers and surface nanostructures assists in the development of new devices based on self-assembled organic molecular films and thin-film photovoltaic cells. A number of physical and physico-chemical techniques can be utilized for this, including: neutron and X-ray reflectometry, atomic force microscopy (AFM); scanning tunneling microscopy, electron microscopy, ellipsometry and X-ray photoelectron spectroscopy. These techniques are all very useful, but can be cumbersome to apply and require large equipment infrastructure which is often not readily accessible.

We have developed a laboratory-bench instrument based on a novel, very high resolution, impedance spectroscopy technique, which also can provide molecular (nanometer) and in some cases atomic-scale resolution of the layered architecture of thin films and molecular nanostructures.

In order to achieve unequivocal analysis of nanostructures at this high level of resolution it is necessary to acquire very high precision measurements of both the phase and the magnitude of the impedance, over a wide range of frequencies. The impedance technology developed by us provides a resolution of 0.001 degrees in phase, and 0.002% in impedance magnitude over a frequency range from < 1 milliHz to 1 MegaHz. This has allowed the detailed characterization of, for example, organic films covalently linked to silicon with a spatial resolution of a single carbon-carbon bond. Results are presented on the application of the technique to a variety of synthetic organic and bio-mimetic surfaces as well as thin film photovoltaic cells.

Introduction

The construction and study of organic films on silicon and metal substrates and electrodes has attracted a great deal of attention, both because of a basic interest in the physical properties of low dimensional structures per sé [1,2], and because such nanostructures have many possible applications as devices, such as organic displays, sensors, memories and charge storage systems [3]. Organic molecular films can be constructed from a variety of molecules with charged terminal groups, redox moieties and binding sites for simple ligands and there is a great deal of interest in exploring the effects of charge (pH), redox reactions and ligand binding on the structure and properties of the films for the development of the next generation of biomolecule sensors.

Additionally, there is much interest also in thin film semiconductor devices and in particular thin film photovoltaic cells. In these devices dynamic interfaces such as depletion layers are formed and these play a cardinal role in the function of the devices.

Structural analysis of surface and interfacial features is an essential element for relating the properties of the nano systems to the processes involved. The molecular structures attached on a substrate can be studied using X-ray (and in particular synchrotron X-ray) and neutron reflectometry [4] and ultra low frequency impedance dispersion techniques [5, 6]. Both the reflectometry and impedance dispersion techniques have similar spatial resolution (of a few Å) but measure quite different properties of the internal structural layers. High resolution electrical impedance spectrometry (EIS) can also probe the depletion layers formed at the silicon surface and detect changes in these regions that result from changes in the composition of the molecular films attached to the surface or from the application of electric potentials. Impedance spectrometry has the further advantage that it can detect depletion layers in the silicon substrate (which are dependent on local intrinsic as well as applied electric fields) and these cannot be detected using the reflectometry techniques.

Impedance spectroscopy and dielectric structure

For a simple homogeneous molecular film on a substrate of, relatively, high conductivity, impedance spectroscopy allows the precise thickness of the film to be determined. This is illustrated in Figures 1a and 1b for a film of octadecane covalently attached to a silicon (111) surface [7]. The strong dispersion in capacitance and conductance at frequencies $> \sim 1000\text{Hz}$ is due to the resistance of the series electrolyte. The film itself can be represented by a capacitance (C) in parallel with a conductance element (G).

The expected dispersion of C and G for such a circuit can be fitted to the actual measured C and G as a function of frequency. The full line in Figure 1b is such a fit and this allows all three parameters (C and G of the film and G of the electrolyte) to be determined. Usually the electrolyte conductance is already known but this can be useful as a check on the fitting routine.

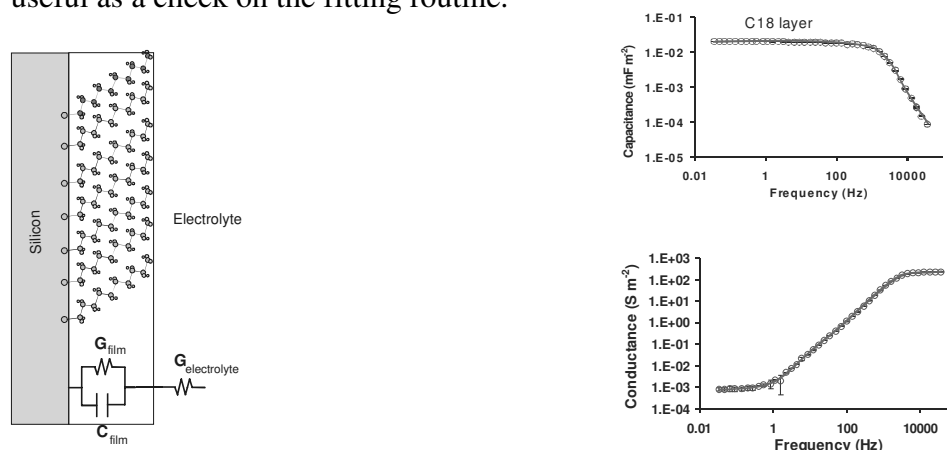


Figure 1a. Schematic of a self-assembled molecular film of a hydrocarbon, covalently attached to a silicon [111] surface, in contact with an aqueous electrolyte. The organic film has a very high resistance (low conductance). The equivalent circuit for such a system is also shown.

Figure 1b. The dispersion of the capacitance (top panel) and conductance (lower panel) of the system depicted in figure 1, with frequency. The strong dispersion for frequencies $> 1 \text{ kHz}$ is due to the series resistance of the electrolyte. The full curve is a plot of the theoretical expected dispersion for the circuit shown in figure 1. This fitting yields the capacitance and conductance of the organic film as well as the conductance the electrolyte. As the dielectric constant of the hydrocarbon is known ($\epsilon=2.05$), the thickness of the film can be determined.

The presence of dielectrically distinct layers within a molecular film or membrane will give rise to a dispersion of the capacitance and conductance with frequency. The impedance dispersion of such films occurs at very low frequencies; typically starting at around 1 Hz and extending over 3 or more decades in frequency. Consider thus a simple homogeneous film and one comprised of two different but homogeneous layers in juxtaposition as shown in Figure 2

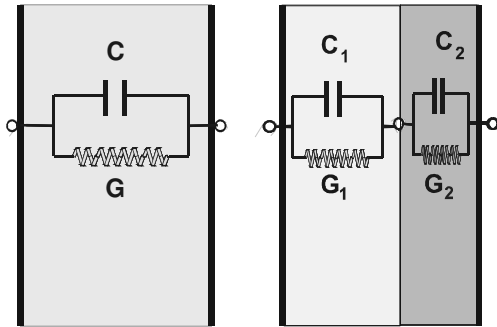


Figure 2. Schematic representation of a homogeneous film and its electrical equivalent circuit as a film composed of two substructural layers with different dielectric and/or conductance properties. The parameters chosen for our illustrative example were: $C_1=0.006\text{F/m}^2$, $G_1= 0.003\text{ S/m}^2$ and $C_2=0.059\text{ F/m}^2$, $G_2= 4.35\text{ S/m}^2$. The values of the capacitance C_1 and G_1 are appropriate for a hydrocarbon film of thickness $\sim 1\text{nm}$ and for the composite film the parameters of the second layer (C_2 and G_2) were chosen to be more appropriate to a polar/charged layer.

For illustrative purposes we have chosen circuit parameters applicable to a simple alkane (hydrocarbon) molecular film (as a single layer system) and one composed of such molecules but terminating in a polar head group.

Figure 3 shows the theoretical dispersion of the impedance expected both for the simple homogeneous film and that for a similar film with a polar head group layer. It is immediately clear that while the impedance of both types of film disperse with frequency, it is not practical to distinguish between them on this basis. However, if the phase of the impedance can be measured independently at each frequency, with sufficient resolution, the dispersion in the capacitance and conductance of the film allows the substructure to be resolved. The dispersion with frequency of these parameters are very different for the homogeneous film and that with the additional substructural layer of polar heads. [8, 9]. This is shown in figure 4.

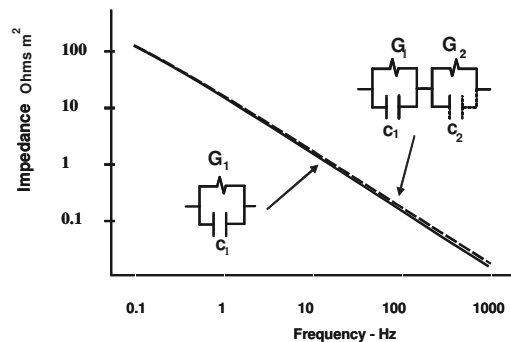
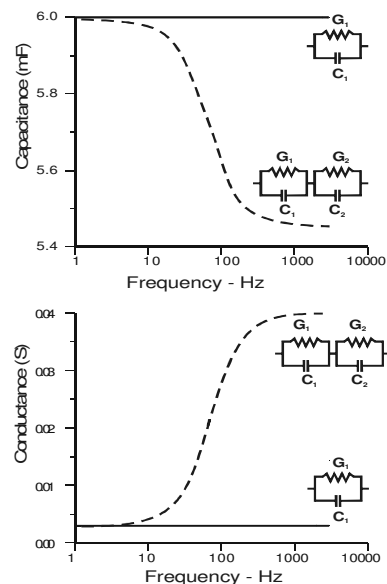
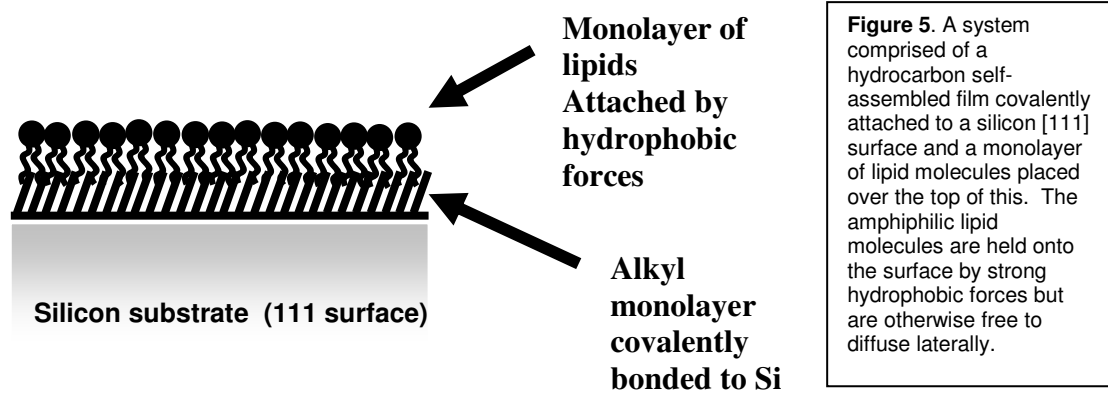


Figure 3. The dispersion of the total impedance with frequency for the single homogeneous film (full line) and the film composed of two layers (dashed line) as shown in figure 2. Note that whilst in both cases the impedance is a strong function of the frequency (note the logarithmic scales used in the plots), the two systems are almost indistinguishable from each other.

Figure 4. The capacitance (upper panel) and conductance (lower panel) as a function of frequency for the system shown in figure 2 of a single homogeneous film (full line) and a film in which there is an additional, polar, substructural layer (dashed line). For the single homogeneous film, the capacitance and conductance do not vary with frequency. For the film containing an additional substructural layer there is a strong dispersion in both C and G with frequency (based on ref [9]).



An example of an actual two layer system is shown in figure 5. In this example a monolayer of lipids was layered onto an alkane (hydrocarbon) film previously covalently attached to a silicon wafer. The lipid molecules are held in place by hydrophobic forces and the system is very stable.



The dispersions of the capacitance and conductance of this hybrid layer in an electrolyte solution is shown in figure 6. The full curves were fitted to the circuit models shown and the fitting yields the values of the individual components that make up the two layer hybrid structure.

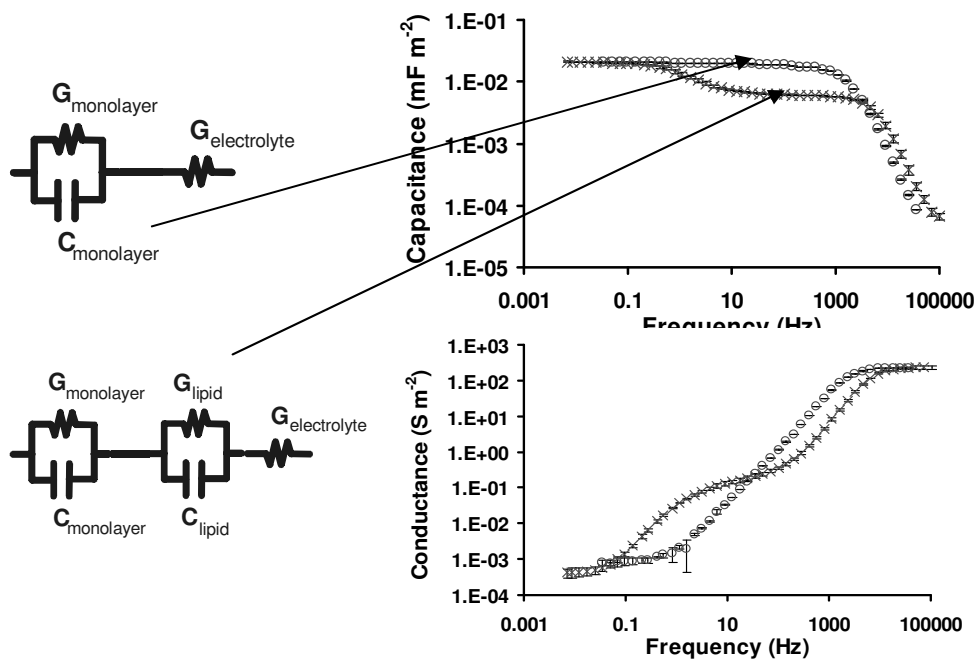


Figure 6. The dispersion of C and G for a 18 carbon alkane film on silicon and a hybrid film containing in addition a layer of lipid (lecithin) molecules held onto the alkane film via hydrophobic forces. Note the additional dispersion (centred around a frequency of ~ 10 Hz) that relates to the presence of the additional substructural layer. The strong dispersion at frequencies > 1 kHz is due to the series conductance of the electrolyte in contact with the films. Data from ref [10]

Photovoltaic cells

The basic structure of a semiconductor photovoltaic cell is schematically illustrated in

figure 7. At the junction of the p and n layers, a depletion layer is formed that has a very low concentration of holes and electrons. This layer therefore has a high impedance and because it is usually very thin (a few hundred nanometers) it has a large capacitance. The bulk p and n type layers also can be each represented by a parallel combination of capacitors and conductance elements. Often the materials are highly doped and hence the conductances are relatively large and because these layers of material are relatively thick, the capacitances are generally small.

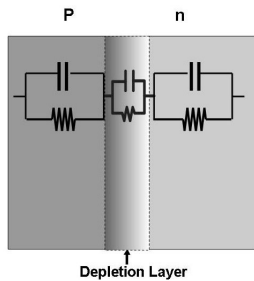


Figure 7. A schematic representation of a basic p - n junction photocell. At the junction of the p and n regions a layer is formed (depletion layer) that is depleted of charge carriers (holes and electrons). The equivalent circuit for such a basic system is also shown

In thin film photovoltaic cells the layers of semiconductor material are much thinner and in particular at least the outer layer is often very highly doped. The conductance of this layer is then so large, compared to the other regions, that it can be eliminated as a circuit element. The depletion layer is then also largely located in the p type region. This type of cell is schematically shown in figure 8. Here we have a two layer system consisting of the depletion layer and the p region outside the depletion layer.

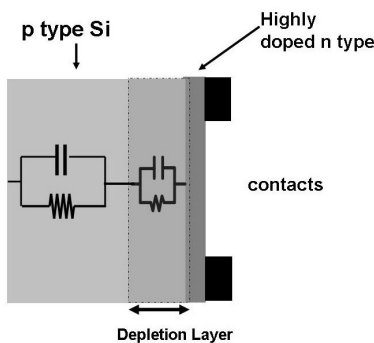


Figure 8. Schematic of a thin-film p - n junction photovoltaic cell. In this illustration the n type region is highly doped and a relatively good conductor. The depletion layer also consequently is large located in the p type material. In crystalline silicon on glass cells, the p type material is also very thin compared to more traditional photocell. The equivalent circuit is now simplified to that of a two layer system.

Impedance spectroscopy can detect and characterize this structure. An example of the dispersion with frequency of the capacitance and conductance is shown in figures 9a and b [11]. The solid line is a fit to the data for a two layer system. The fit is excellent for frequencies >1 Hz and this allows the conductance and capacitance and hence the thickness of each layer to be determined (using the known value of the dielectric constant of silicon).

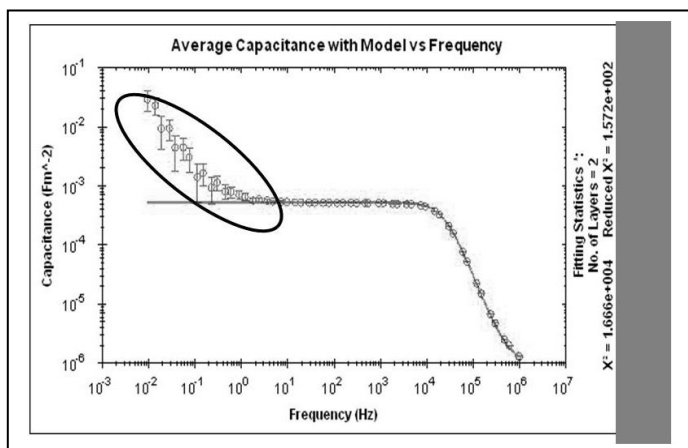
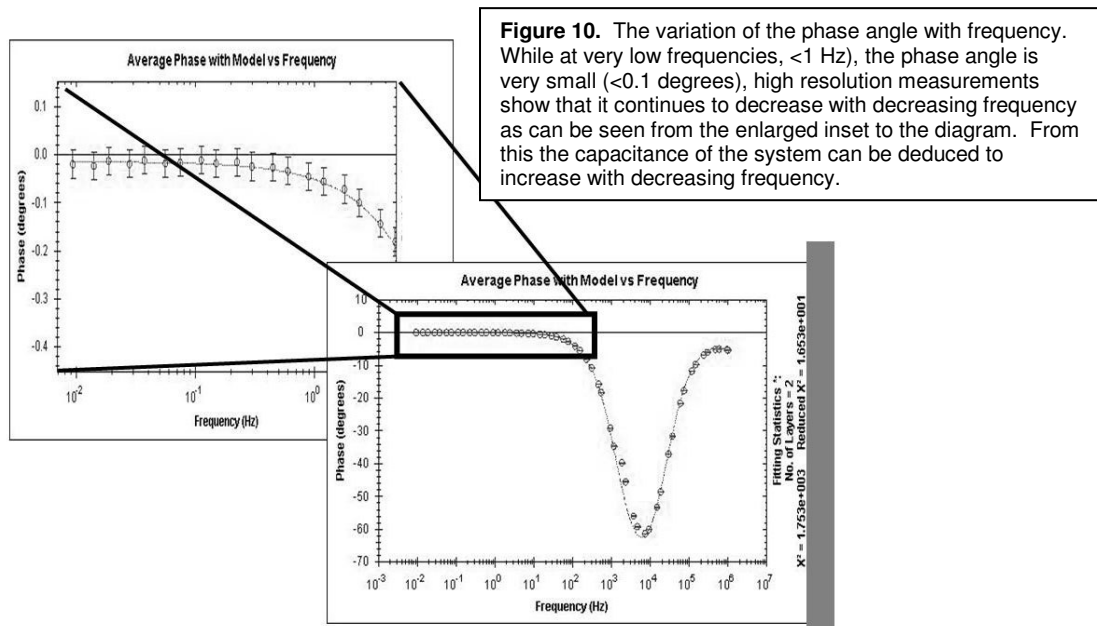


Figure 9. The dispersion with frequency of the capacitance for a thin-film crystalline silicon on glass photovoltaic cell. The full line is a fit to the two layer model shown in figure 8. Note the excellent fit for frequencies >1 Hz. From this the thickness and conductance of each of the two layers depicted in figure 8 could be deduced. For the dispersion of C below 1 Hz (encircled region) a simple dielectric sandwich model cannot account for the very strong dispersion at these low frequencies.

The capacitance determined at very low frequencies, however, continues to rise very rapidly as the frequency decreases. This is not due to the presence of additional layers but rather is typical of a phenomenological impedance element that arises from diffusion polarization effects. The measured additional dispersion in capacitance might at first be dismissed as a measurement artifact; since the phase angle rapidly approaches zero with decreasing frequency, see figure 10. However, with high resolution instrumentation it can still be determined and allows the capacitances to be determined.



At very low frequencies the concentration of the minority carriers have oscillatory spatial components that are established because changes in concentration driven by the applied AC current are diffusion limited. This effect does not occur at high frequencies as there is insufficient time during each half cycle of AC to substantially alter the carrier concentration. This *phenomenological* impedance manifest as a frequency dependent capacitance element, shown in figure 11 and is sometimes referred to as a *charge-injection* capacitance. As it relates to diffusion effects of the carriers, it may be of relevance to the development of new devices.

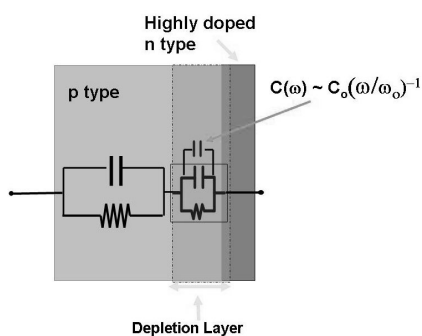


Figure 11. The phenomenological impedance element arising from diffusion polarization effects at the boundary of the depletion layer leads to a frequency dependent element (capacitance). Such an element manifests only at very low frequencies where diffusion limited profiles of charge carriers are established when low frequency AC currents are passed through the system. At high frequencies there is insufficient time for such spatial, time dependent, concentration profiles to be established.

Incorporation of such a frequency dependent capacitance as a phenomenological element allows the capacitance at very low frequencies to be accounted for. This is shown in figure 12. High resolution impedance spectroscopy thus allows the parameters for such a thin-film photovoltaic cell to be completely characterized.

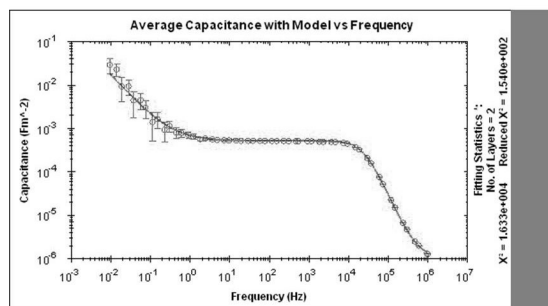
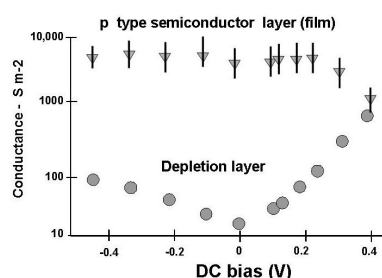


Figure 12. The measured capacitance dispersion and theoretical fit incorporating a phenomenological impedance element (frequency dependent capacitance) which dominates the dispersion at frequencies < 1 Hz.

The variation of all of the separate parameters with DC bias (either externally applied or through exposure to light) can then be investigated and an example is shown in figure 13.

Figure 13. The variation of the conductance of the depletion layer and the thin-film p type region as a function of DC bias. These parameters could be determined directly from high resolution impedance spectroscopy measurements.



Summary

High resolution impedance spectroscopy is a very useful technique to probe the substructure and substructural properties of molecular thin films and p-n junction devices photovoltaic cells. It forms a powerful adjunct to other techniques such as X-ray and neutron reflectometry and ellipsometry.

References

- 1 Scandurra, A., Renna, L., Cerofolini, G. and Pignataro, S. S. I. A., 34, 777., 2002, *Surf. Interface Anal.*, **34**, 777
- 2 Stewart, M. P. and Buriak, J. M., 2002, *Comments on Inorganic Chemistry*, **23**, 179
- 3 Lee, W., Kim, E. R. and Lee, H., 2002, *Langmuir*, **18**, 8375
- 4 Penfold, J. and Thomas, R. K., 1990, *J. Phys.: Condensed Matter*, **2**, 1369
- 5 Coster, H. G. L., Chilcott, T. C. and Coster, A. C. F., 1996, *Bioelectrochemistry and Bioenergetics*, **40**, 79-98
- 6 Coster, H. G. L. and Smith, J. R., 1974, *Biochimica et Biophysica Acta*, **373**, 151-164
- 7 Böcking, T., James, M., Coster, H.G.L., Barrow, K.D., Chilcott, T.C (2004) *Langmuir* **20**: 9227-9235
- 8 Coster, H. G. L. and T. C. Chilcott (1999). In "Electrochemistry of membranes" : T.S. Sorensen : *Marcel Dekker, New York* 749-792
- 9 Coster, H. G. L., T. C. Chilcott and A. C. F. Coster (1996) *Bioelectrochem. Bioenerg.* **40**: 79-98.
- 10 Chilcott, T.C., Coster, H.G.L. and Böcking, T., (2007). *Biophys. Rev.L.* **2**, 191-199
- 11 J. Wong, H. G. L. Coster , T. C. Chilcott, N. Haufe and M. Green. (2009) *in preparation*