MINUTES

META Kick-off Meeting

1st June 2011

held at Centre NAST, University of Rome Tor Vergata (I)

During the kick off meetings researchers from the two European and American partners presented their organizations expertise in the areas relevant to META. The various research challenges that needed to be addressed within the program were discussed. The themes are focused in the area of **DNA motherboards, (WP1) selective adhesion of peptides (WP1) and grown LSCM films on various substrates (WP2).**

During the **meeting**, the partnership, management, communication procedures have been established, and all relevant research issues have been setup, thus ensuring a highly successful project. It was decided to set up a web site for the META project in order to share ideas and share results obtained over the period of the project.

This meeting followed definition of the base elements for the project and revised the project planned activities, and provided the opportunity to discuss the role of each team member.

Activities within META, June 1st 2011

WP1: Italian researchers have been working on the selective adhesion of peptides onto Cr, Ti and ZnO both experimentally and theoretically. Simulations of the peptides folding are being run while the experimental tests on the adhesion have been only partially successful (the specific peptide for Ti also bind Cr although with lower frequency).
DNA grid assemblage is in progress, we should know if it is successful in a short time.
Piero Morales has e-mailed Mike in order to define the more convenient week in October for a visit to ORNL. Fixing the schedule as soon as possible is an important issue in order to get lower flight fares.

Summary of scientific issues (P Morales, M. Simonson)
Participants to discussions for WP1: T. Hianik, B. Sumpter

DNA motherboards assembly:
Two different possibilities for selfassemblage of DNA based nanostructures are envisaged. Both can be used as "motherboards" for selfassemblage of protein "plug-in" components. Two different general approaches are proposed:

1) Selfassembly of DNA cross shaped elementary "tiles", each made of 9 different oligonucleotides, to be joined together in larger structures via suitably designed "sticky ends" of the elementary tiles;

2) Selfassembly of planar sheets of DNA obtained by one single long single DNA strand folded in the designed shape by means of a number of oligonucleotide "stapling" sequences that hold together the structure at the predesigned sequence locations

Use of materials specific adhesion peptides to address the motherboards onto the desired nanopads is not yet an established technology, and this workpackage aims at offering a contribution to such technology. But in order to attempt such option, it is important that the interaction of the rest of the structure to the substrate is minimal, as non specific interactions negatively affect the correct selfpositioning of the motherboards on the substrate.

We have decided to start the work by use of the first "tiles" based concept, implying a smaller contact surface with the substrate, in spite of the lower yield of selfassemblage as resulting from existing literature. Furthermore this gives us the possibility to easily reduce the size of the selfassembling motherboard by assembling only intermediate sized structures, down to a minimum square structure of approximately 20 nm side.

The approach can be changed in the subsequent project years, should the yield of assemblage of the tiles based structure be too low for establishment of a practically viable technology.

The oligonucleotides sequences that will selfassemble into component "tiles" and then into square grids defining an addressable cartesian coordinates system have already been investigated and designed, and they are ready to be synthesized. The following step will be an evaluation of the yield of correct and complete synthesis and a PAGE purification of all sequences.

Materials selective adhesive peptides:

The recent literature reports of several examples of materials selective oligopeptides that when displayed on the P3 or P9 end proteins of the M13 bacteriophage, exhibit a strong specific adhesion with respect to the materials they have been selected on. Some of these peptides have been demonstrated to be vey selective. Endowing the cornering "tiles" of the motherboards with such peptides (suitably conjugated to the "arm" oligonucleotides of the chain) may thus allow specific addressability and orientation of the DNA nanostructure on nanopads of specific materials fabricated on the surface. Among these peptides we have selected three for their relevance and for their specificity:

1) Peptide specific for Titanium oxide in the anatase phase
2) Peptide specific for chromium (or better native oxide of chromium)
3) Peptide specific for zinc oxide

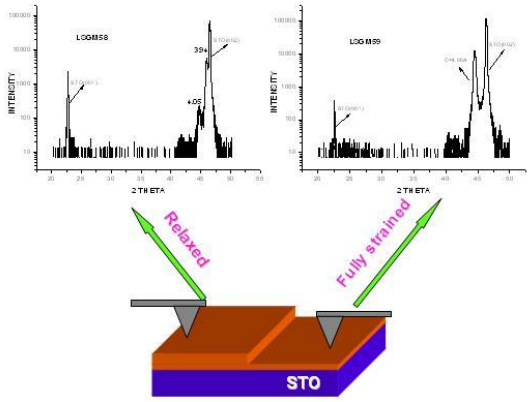
Previous experience of our group on molecular dynamics simulation of peptides specific for graphitic carbon will give us a sound base for tackling the other peptides that we have chosen.

On the other hand experimental work based on fluorescence of chromophore molecules tagged onto our peptides are under way and will allow us to compare adhesion as calculated through the MD simulations to the real case of peptidic sequences. It should be emphasized that the experimental data available from the literature concern peptides displayed on the P9 protein of the whole viral structure, which may well

Summary of Scientific discussion (Giuseppe Balestrino and Silvia Licoccia)

Participants to discussion for WP2: I. Anderson, C. Andreani

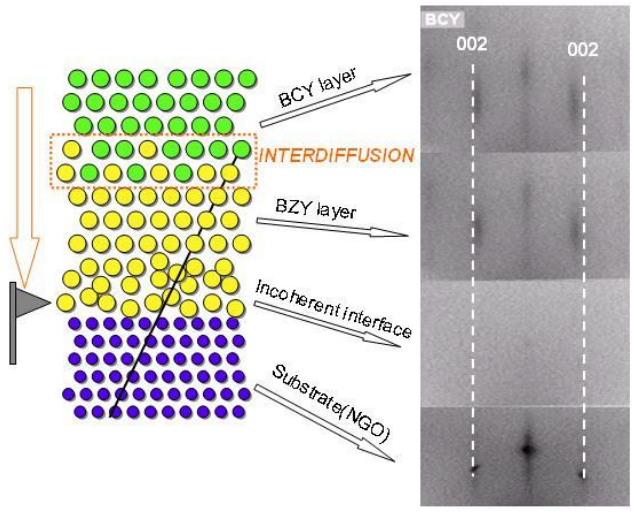
LSCM films on various substrates have successfully grown at NAST Centre. LSCM (La1-xSrxGa1-yMgyO3) is a promising ionic conductor with the perovskite structure. Best structural quality was obtained for LSGM films grown on STO substrates. However, due to the high contribution to conductance from the substrate, in this case we were unable to single out the film contribution by electrochemical impedance spectroscopy (EIS). Conductance was measured by EIS for LSCN films grown on both STO buffered MgO and NdGaO3 substrates. Furthermore, films grown on STO remain fully strained with a very high crystallographic quality up to a thickness of few hundreds of nanometres. Above such thickness the epitaxial strain relaxes and the crystallographic quality gets worse. Therefore we propose (a) to measure the local ORR/OER and oxygen vacancy diffusion in fully strained, high quality LSGM and compare the results with those obtained for relaxed LSGM (see figure).



We are growing BZY and BCY (both proton conductors with the fluorite structure) individual layers and heterostructures following the evolution in site by Reflection High Energy Electron Diffraction. It is clearly seen that the interface quality is poor due to the large misfit between the film and the substrate. On the other the structural quality is healed at a larger thickness. It is known that a defective interface can modify strongly the proton conductivity, possibly enhancing it strongly. However, it is very difficult to probe this effect directly by standard EIS measurements. Would it be possible to follow the approach suggested in the following figure, namely to carry out SPM measurements along the growth direction? This would give a direct insight into the interface properties.

In this scenario It is important to add that the NAST Centre group is ready to take care of the necessary EIS experiments and fuel cell tests to correlate SPM and macroscopic data. Neutron scattering experiment at SNS on SEQUOIA and BASIS beamlines are also planned to study the dynamocs of the protons within the BZY powder.

To follow Stephen's e-mail, the primary two projects that will be of interest for us at this point will be (a) quantitative ESM measurements and (b) superionic interfaces. That said, we are obviously open for ideas if there are specific samples you are interested in looking at.



Further Issues to tackle

A. *For quantitative measurements, I note that ESM imaging works remarkably well for a broad variety of materials (we have data on a large number of Li-ion materials including LiCoO2, lisicon, Si, and oxygen conductors including YSZ, several bicrystals, (LaSr)CoO3, and (LaSr)FeO3). However, it is very obvious that this technique will not be broadly adopted by electrochemical and SOFC communities until it is quantifiable - if not on the level of EIS, but at least at some.*

In this respect, it looks like SDC samples from your group offer best reproducibility and least effect of topographc variations, as well as some interesting and nontrivial signatures in the loop shape, and hence can be a natural target for these studies. To develop it further and should you be interested, I was wondering if you will be able to provide us with samples of different thickness and known materials parameters (ideally, ionic and electronic conductivities vs. temperature - so we can extrapolate these to RT)

Yes we can provide you SDC (or different materials) films having different thickness and grown on different substrates.

- kinetic information on ORR on clean (and may be Au and Pt fictionalized) surfaces (ideally, temperature and pressure dependence of exchange current density, possibly temperature dependent polarization relaxation data, kinetic data) [see example of papers where they are acquired]

- also, would you know what is the propensity of these materials for proton conduction? The reason for these is that ESM experiment is almost equivalent to probing electrocatalysis on a single nanoparticle (either deposited on a surface and contacted by tip, or nanoparticle being a tip). It will be very tempting to extend this analogy to quantitative models. Can you let us know which of these experiments are within the scope of your program?

We do not have direct experience on functionalizing surfaces or measuring ORR kinetics. We have to look deeper into this. Of course we can measure proton conduction by EIS and the experiments are within the scope of the project.

B. For superionic interfaces, the idea is significantly simpler and involves ESM mapping of the interface area. Can you make such samples (by polishing cross-section) of multilayers and bilayers, and are they available at this point?

See point 1 of our email (above). Multilayers are already available. Unfortunately we do not have the know-how and the necessary technologies for polishing cross section.

C. In all cases, we have long standing collaborations with several theory groups, most notably Anna Morozovska at Ukranian Academy of Sciences and Francesco Ciucci currently at Heidelberg (I have

attached his thesis, since the problem of electrode he considered is very similar to ESM in formulation). Does their inclusion in the collaboration present any concern for you?
No problem.

D. Much more philosophic question - it seems that there is a certain disagreement in SOFC community on whether ORR/OER should be described through Nernst-type analysis, or Butler-Volmer type kinetics. What is your feeling about it?
It is decided that these issues will be tackled and results will be presented in forthcoming meeting.

The next META meeting will take place in OCTOBER 2011 and will be hosted by the Batelle, CNMS partner Oak Ridge National Laboratory, Knoxwille (US).

Rome 10 June 2011