



DOCTORAL PROGRAM IN MATERIALS ENGINEERING

Chair:
Prof. Chiara Castiglioni

The courses of the Doctoral Program provide Ph.D students in Materials Engineering with a common, basic knowledge on Materials Science and Technology, followed by a specialized training in specific fields. The objective is to combine the theoretical knowledge with the skills required by technology in order to form qualified researchers who can manage the design, manufacturing and use of traditional and/or new materials.

Contents of the Doctoral Program

The Doctoral Course covers the following areas:

Polymers and composites

Cements and ceramics

Metals

Biomaterials and materials for biomedical applications

Processing and characterization of advanced metallic alloys

Corrosion and durability of materials

Innovative materials for civil and industrial engineering

Materials Characterization (Microscopies, Scattering, Spectroscopy)

Modelling and theoretical approaches to the study of materials structure and properties

Micro and nanostructured materials

Functional materials for applications in photonic, electronic and sensors

Surface engineering and advanced coatings

Materials for industrial design

Meta-materials

Transformation of materials

Material for Cultural Heritage

The courses face immediately advanced issues both in the main and elective courses. Different curricula are offered, which will be activated on the basis of the decisions of the faculty. The Doctoral program is characterised by high flexibility, in order to satisfy the needs of students that have to develop their research activity in different thematic areas. For this reason each student submit to the Faculty a "Curriculum" to be approved. The Courses offered deal with theoretical, experimental and modelling aspects. Several Courses comprise workshops and seminars, with the participation of invited internationally celebrated speakers. Students can use the most modern facilities for materials synthesis, processing and characterization available at the Politecnico di Milano or in other research laboratories. The research activities related to the Ph.D. theses develop, full time,

along the three years of the Ph.D. courses. Stages in industries or in national laboratories in Italy or abroad are offered. Each Ph.D. student are supervised by a professor of the faculty: the faculty evaluates the progress of his research activity and at the end of each year expresses a judgement on the continuation of the work for the subsequent year. At the end of the third year the Ph.D. student presents and defends, in a public hearing, his thesis work with a jury formed by three experts.

The Ph.D. student is strongly encouraged to attend at national and international meetings and present papers in his specific field. The Ph.D. student is also assigned to give seminars on topical issues and/or to lecture on the specific fields of his research or on the cultural aspects related to his thesis.

The Doctoral School requires the acquisition of 180 credits (in 3 years) :

- at least 30 credits must be obtained through attendance at Doctoral Courses (with positive evaluation in the examinations); in addition, attendance at National and International Schools are strongly encouraged.
- the remaining credits will be assigned on the basis of the research activity necessary to the development of the Thesis project.

Faculty:

The faculty is constituted by Professors from several Departments of Politecnico di Milano:

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Professional skills achieved by PhD in Material Engineering:

The industrial world depends necessarily on a great variety of materials. Nowadays, it is easy to outline two industrial needs: i) development and innovation in the production, processing, application and conservation of traditional materials; ii) development of innovative materials for the production of new manufactured goods or devices to cope with the growing demands of modern technologies. Since these two kinds of industrial needs require specialized people a few specialized curricula are offered. On the other hand, the capabilities acquired through the courses, the research work and the teaching activity assure an adequate preparation to the academic career.

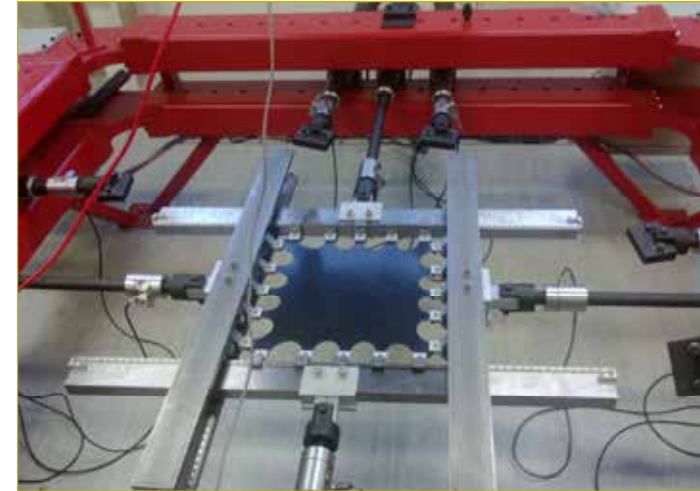
MECHANICAL CHARACTERIZATION OF ELASTOMERS UNDER QUASI-STATIC AND DYNAMIC BIAXIAL LOADING CONDITIONS

Roberto Calabrò - Supervisor: Marta Rink

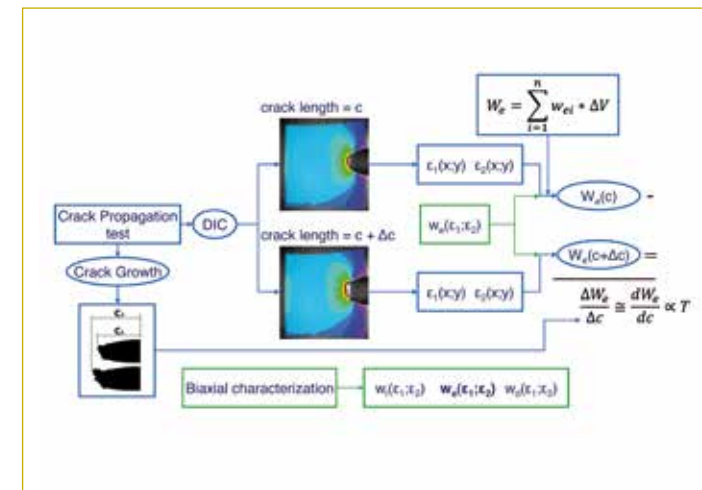
The research activity was focused on the determination of a fracture mechanics energy based parameter suitable for elastomers when subjected to biaxial loading conditions. Although for some simple geometries such as SENT or pure shear, simple experimental methods for evaluating the energy release rate or the J-integral for highly non-linear materials as elastomers can be found in the literature, for the case of biaxial test configurations these are not available. Two specific techniques were developed to evaluate the tearing energy, which can be used for this test configuration, by using direct and indirect calculation methods. Both calculation techniques require an accurate calibration of the constitutive model of the material. Constitutive equations for hyperelastic materials, which can describe the behavior under different stress states and high strains generally contain a large number of parameters. Therefore in order to obtain a sound parameters set experimental data under different stress states and high strains are required. Two loading conditions were considered, dynamic and quasi-static. For dynamic stress-strain characterization and fatigue crack propagation

tests a biaxial testing machine purposely designed for rubbers was used during a six months stay at "Leibnitz Institut für Polymerforschung Dresden e. V. (IPF)". A direct technique for tearing energy evaluation, based on full-field strain measurements performed with the digital image correlation technique, was proposed and successfully tested, although the obtained results need to be confirmed with further stress-strain and fatigue characterization tests. For quasi-static tests a biaxial dynamometer designed for textiles was adapted for testing elastomers up to high strains by designing an ad hoc clamping system. In this case an indirect technique based on finite element simulations was used to determine the tearing energy. Unfortunately, the production of the clamping system has taken longer time than expected, and was available for testing only from April 2013. For this reason it was possible to perform a stress-strain characterization but only a few fracture tests. The determination of material parameters even using characterization data from different biaxial load configurations is still not satisfactory. Nevertheless, lately some attempt to calculate the tearing energy with the finite element method has been done and the results obtained are

encouraging. Much attention has also been devoted to obtain an optimal speckles pattern for digital image correlation. It was then possible to extensively apply this technique in the thesis work.



1. The designed clamping system mounted on the CLUSTex biaxial tester with a specimen stretched in equibiaxial extension.

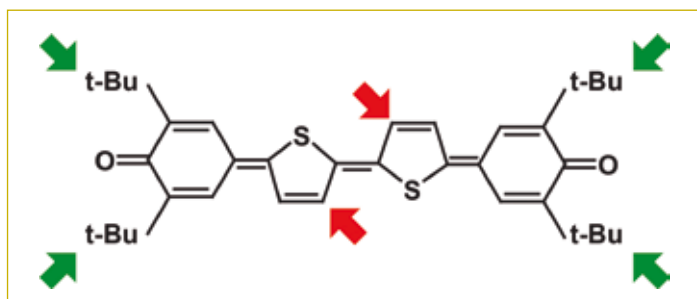


2. Flowchart of the proposed technique for tearing energy evaluation from strain full-field measured by DIC.

STRUCTURE TO PROPERTY RELATIONSHIP IN LOW BANDGAP CONJUGATED PHENOQUINONES FOR THIRD GENERATION SOLAR CELLS

Letizia Colella - Supervisor: Chiara Bertarelli

Though photovoltaic market is led by silicon technology, due to the high cells efficiency and long-term stability, the good performance attained by the organic solar cells has opened new opportunities for the production of light, low-cost and possibly flexible devices to be implemented in many daily use items. In this framework, novel phenoquinone oligomers have been designed and synthesized for their possible use as third component in bulk-heterojunction solar cells. These phenoquinones demonstrate peculiar electronic features: by a combined experimental (NMR, UV-vis, Raman and Resonant Raman) and theoretical study, an unexpected turning of the quinoidal into a biradicaloid character by increasing the molecular length of a homologous series of thiophene-based quinoidal species has been observed. To better highlight the relationship between the effective conjugation over the molecular backbone and the biradicaloid character, heterophenoquinones with the bithienylene core replaced with different linear or condensed polycyclic rings have been also synthesized. The investigation of these new materials has shown that naphthalene and thienothiophene as central structures lead to an electronic



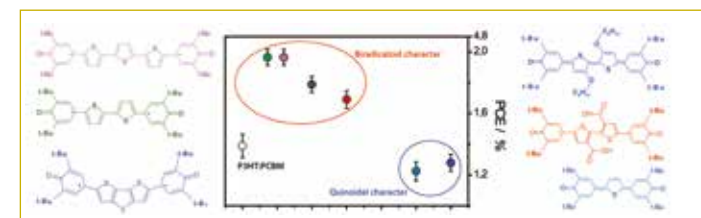
1. Molecular structure of QBT. The arrows show the sites of functionalization: 3,3'thiénylic position (red) and 2,6-phenyl positions (green).

character which is intermediate to quinoidal and biradical, whereas the biradicaloid structure is favored when longer condensed rings and oligoaryls are introduced. Derivatives containing fluorene and homologous species, which were expected to reflect the same exhibit a quinoidal character due to their limited conjugation have not been deeply investigated due to their poor stability. Moreover, the introduction of donor substituents on the 3,3' positions in the central core of the biradicaloid material of reference, namely 5,5'-bis-(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-2,2'-dihydroxy bithiophene (QBT, figure 1), turned into a stabilization of the quinoidal ground state structure without affecting the effective π conjugation. This represents a new insight into the general class of thiophene-

based quinoidal molecules, where only the dependence of the biradicaloid structure on the effective conjugation length (e.g. E_{gap}) has been so far reported, and gives the relevant opportunity of a separate control of the electronic character of the ground state over the optical bandgap.

On the basis of these results, the influence of withdrawing substituents on the electronic structure has been also investigated, as well as the introduction of donors and/or acceptors on the lateral phenone moieties (see figure 1). Heteroquaterphenoquinones bearing acetal and carboxylic acid in the central core are characterized by the same Raman fingerprint of the unsubstituted one, leading to the hypothesis that the introduction of electron acceptor groups stabilizes the biradicaloid

character. Surprisingly, preliminary results have highlighted that the introduction of electron active substituents on the lateral phenones has an opposite influence on the overall peculiar electronic behavior of these materials, compared to the introduction of electron donor/withdrawing groups on the central core. Therefore, it has been demonstrated that electronic character of heterophenoquinones is affected not only by the nature of electron active substituents, but also by the position of the molecular backbone they are linked to. Considering the peculiar intense light absorption red shifted of these quinoidal species with respect to the state of the art binary P3HT:PCBM bulk heterojunction composite, they have been studied as a third component for the development of organic solar cells. An increase in efficiency (PCE) around 47%, by adding only 0.6%, of 5,5'-bis-(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-2,2'-dihydroxy bithiophene (QBT), has been actually gained, while a further addition is detrimental for the device performances. Ternary mixtures with different ratio between components have been characterized by means of UV-vis absorption spectroscopy, fluorescence spectroscopy,



2. PCE values distribution. Each spot corresponds to a single ternary solar cell based on the binary blend P3HT:PCBM and an additional 0.6% of a phenoquinone. The reported molecules correspond to the third component used in the devices showing a spot of the same color.

ultrafast UV-vis transmittance spectroscopy, AFM, and differential scanning calorimetry to investigate the origin of this enhanced efficiency. A significant better harvesting of red light, to extend the light harvesting of the P3HT:PCBM system has been ruled out due to the small amount of the quinoidal species, whereas an effect of the third component on P3HT supra-organization and blend morphology has been demonstrated. Keeping fixed the relative content of P3HT:PCBM:Quinones which gave the best efficiency enhancement, some other quinoidal materials among the series synthesized have been tested: it was found that the majority among biradicaloid structures show better performances, with an enhancement both of Fill Factor and PCE, while the introduction of quinoidal structures turns into a worsening of P3HT:PCBM

efficiency (Figure 2). The proximity between the LUMO levels of the biradicaloid species and the fullerene derivative, enables an interaction between the two components through a spin-flip mechanism, which should prevent the recombination of polaron pairs (PP) at the donor-acceptor domain interfaces. This finding is worthy to remark, as definitely demonstrates that the role of the quinones is not limited to a morphology improvement of non-optimal P3HT-PCBM microstructures, but their peculiar biradicaloid character actually takes part in exciton dissociation.

DIFFUSION AND TRAPPING OF HYDROGEN IN PIPELINE STEELS

Ehsan Fallahmohammadi - Supervisor: **Prof. Fabio Bolzoni**

The presence of hydrogen into steels is well known to be detrimental, in particular for ferritic steels: typical phenomena are stress corrosion cracking due to "hydrogen embrittlement" mechanism, worsening of mechanical properties (i.e. significant decrease of ductility and /or fracture strength), delayed fracture or irreversible damage (like blistering). The thesis deals with hydrogen diffusion of two pipeline steels, a carbon-manganese (API 5L X65) and a low alloyed (ASTM A182 F22), in three different metallurgical microstructures (bainitic, martensitic and ferritic-pearlitic) and mechanical states (plastically deformed and under the fatigue loading), compared with those obtained on C-Mn steel not produced for sour service (API 5L grade B). Tests were carried out by electrochemical permeation techniques proposed by Devanathan and Stachurski with three different diffusion coefficient measurement methods: 1) standard ISO charge method; 2) partial charge/discharge method (after long polarisation); 3) discharge method. The charging method enabled to measure an apparent diffusion coefficient, influenced by both lattice diffusion and trapping. The diffusion coefficient

obtained by partial charge/discharge and the first stage of complete discharge method was close to the one of pure iron, then it can be reasonably assumed to be the lattice diffusion coefficient of hydrogen, dependent only on the hydrogen migration processes in the crystal lattice regular sites. When the microstructure was modified by means of thermal treatment, the lowest diffusion coefficient was found for martensitic, intermediate for bainitic and the greatest one for annealed steel. The highest lattice hydrogen concentration belongs to the martensitic steel. Since the transport phenomena are hindered in martensitic steel, the hydrogen concentration can be locally increased thus rendering the steel more susceptible to cracking. However, the cracking susceptibility and related consequences cannot be easily interpreted by diffusivity of hydrogen alone. D lattice was reduced in plastically deformed steel, and this effect was more evident with increasing level of plastic strain. The binding energy of reversible traps obtained by fitting procedure based upon the McNabb and Foster and Oriani's models was very similar (-34.4 ± 2.0 kJ mole⁻¹) and can be

associated with dislocation or grain boundaries

Keywords: pipeline steels, microstructure, plastic strain, hydrogen diffusion, lattice diffusivity, trapping, H-Trapping binding energy.

DEVELOPMENT OF ANTIBACTERIAL SURFACE MODIFICATION TREATMENTS FOR TITANIUM TO IMPROVE THE OSTEOINTEGRATION

Teresa Gatti - Supervisor: Chiara Bertarelli

Conjugated organic materials are a promising alternative to the traditional inorganic semiconductors for electronics and optoelectronics applications, thanks to the peculiar optical and electrical properties strictly related to their chemical structure. Organic devices can be ideally scaled down to molecular dimensions; moreover, they can be developed as low cost, flexible, large area systems. In this contest, the study of molecular design and the comprehension of structure-property relationships are essential for the development of more efficient devices and the structural versatility of thiophene motifs provides tailor-made scaffolds for the synthesis of conjugated materials with tunable optic, electronic and redox features.

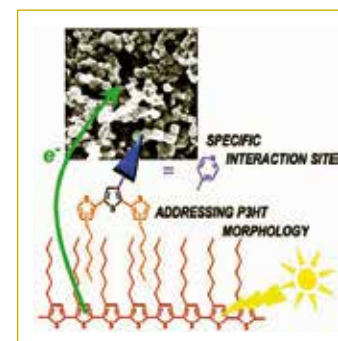
The PhD research activity has mainly focused on the development of thiophene-based materials for third generation, hybrid organic-inorganic photovoltaic cells. In these devices, conjugated polymers are the organic component which absorbs light and transfer the photo-excited electrons to a nano-crystalline metal oxide semiconductor, either titanium dioxide or zinc oxide, with the role of transporting the electrons to the external circuit. Although solid state hybrid photovoltaics

has great potential for offering a cost-effective approach to convert solar energy into electricity, performances so far obtained are rather low, due to problems at the organic/inorganic interface.

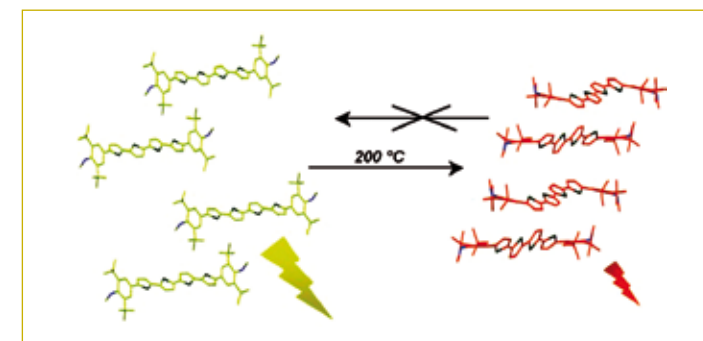
In this study, the efficient infiltration of regioregular poly-alkylthiophenes into the mesoscale porosity of hierarchical TiO₂ nanostructured films was first demonstrated by means of XRF and GD-OES depth profiling analysis. A light-absorbing polymer layer of nanometric thickness, matching the exciton diffusion length, was distributed onto the surface of the rigid inorganic substrate throughout the whole thickness. Separated charges are effectively generated upon photo-excitation of this hybrid junction; however, a fast charge recombination also takes place.

To overcome this relevant drawback, the use of a light-harvesting polymer substituted with specific chemical functionalities, which can better interact with the polar surface of titania, was devised. The functional groups were introduced either at the end of the lateral alkyl chains or directly onto the conjugated backbone of a poly-3-alkylthiophene. Only the second strategy afforded polymeric materials with good solubility in common organic solvents to be processed.

The derivative bearing ethyl ester pendant moieties was selected as photosensitizer for the standard nanocrystalline TiO₂ paste. The ability to bind more tightly to the inorganic scaffold when compared to its un-functionalized polymer precursor was demonstrated but, contrary to what expected, a solar cell made of these active components showed a strong decrease in the photon to electron conversion efficiency with respect to the state of the art device. This result was ascribed to the gap opening and the lack of crystallinity caused by the introduction of bulky substituents, which worsens light harvesting and hinders the efficient transport of positive charges towards their electrode. To hamper charge recombination and enhance exciton splitting, an alternative strategy was envisaged, consisting in engineering the hybrid interface by insertion of a proper molecular interlayer, able to address selective intermolecular interactions both with the polymer and the metal oxide. A number of specific chemical moieties was considered: novel α -oligothiophenes bearing pyridyl functional groups were designed, synthesized and tested as interlayer in P3HT/nc-TiO₂ photovoltaic devices. The pyridyl functionality was expected to ensure specific interaction



1. Schematic representation of the structural polymorphism and correlated photoluminescence properties in a bulky-group substituted phenyl end-capped quaterthiophene.



2. Schematic representation of the use of novel α -oligothiophene interlayers in poly(3-hexylthiophene)/nano-crystalline titanium dioxide hybrid solar cells.

for the inorganic matrix while thiophenes, aimed at inducing supramolecular ordering of the conjugated polymer onto the hybrid interface (Figure 1). The analysis of their performance in solar cells highlights the significant role of molecular configuration, given by the type and relative position of the substituents. So far, the best results were achieved with the 3-(4-pyridyl)thiophene, which nearly doubles solar cell efficiency if compared to a control device without any interlayer. Nevertheless, the study of the entire homologous series of interlayers has provided, useful guidelines for the future development of more effective molecular interlayers. As a side project, completely unrelated with the leading

subject of the PhD, the optical properties of phenyl end-capped oligothiophenes were examined, in relations to their molecular configuration. The possible application of these materials in organic light-emitting devices was preliminarily evaluated by measuring their photoluminescence quantum efficiency in different aggregation states. Solid-state structural analysis was performed in order to determine the influence of molecular conformation and packing on the optical properties. Interestingly, one of these materials was found to exist in two stable polymorphs that can be selectively produced, having different photoluminescence features (Figure 2). This study has evidenced the role of

the side-groups, together with a stringent control over crystallization conditions, to obtain well-defined molecular packing of the aromatic backbone, which in turn may allow a modulation of light-emission.

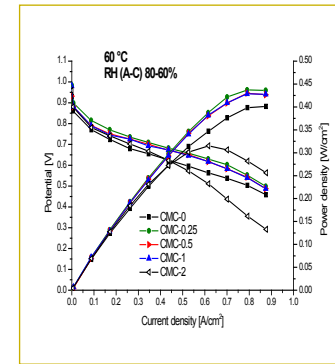
NOVEL MICROPOROUS LAYERS FOR ENHANCED PERFORMANCE AND EFFICIENT WATER MANAGEMENT IN PEM FUEL CELLS

Saverio Latorrata - Supervisor: G. Dotelli

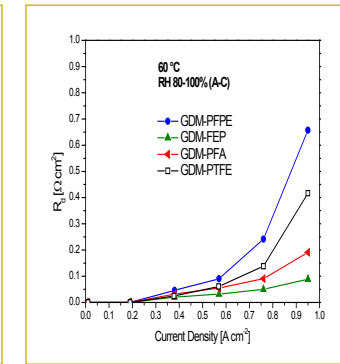
In recent decades Polymer Electrolyte Membrane (PEM) fuel cells have attracted scientific community attention for use as power sources in mobile and stationary applications due to low related emissions and high power densities reached. Thus, several efforts have been spent in order to develop technologically advanced materials for improving electrical performances. Gas diffusion media (GDM), consisting of a macroporous carbon cloth-based gas diffusion layer (GDL) and a microporous layer (MPL), plays a crucial role on reactant gases diffusion and water management in PEM systems. In particular, MPL is made from a carbon black-based ink and coated directly onto GDL. Such a coating improves the smoothness of the GDL surface allowing a better contact with the catalytic layer and introduces micropores which make water condensation and removal easier. Hence, GDM has to be hydrophobic in order to fastly eliminate excess water deriving from cathodic reduction reaction. Currently, both GDL and MPL are made hydrophobic by using a PTFE dispersion in preparation routes. The aim of the PhD research was to prepare, characterize and test different innovative GDMs, focusing both on ink preparation for MPLs deposition

and on novel hydrophobization treatments, with the final purpose to improve global device performances in terms of cell efficiency and maximum output power reached and to reduce diffusive limitations. Firstly, time-stable and repeatable inks were developed; particular attention was paid on rheological behaviour since a shear thinning behaviour is necessary to make inks suitable for blade coating, that was the selected technique for MPLs deposition. For this purpose, a well-known viscosity and stability controller, carboxymethylcellulose (CMC) was added to a traditional ink formulation based on carbon black powder, PTFE, TritonX100 as a surfactant and water as a solvent. Several concentrations of CMC were employed and two different depositions were adopted: a single layer with CMC and a double layer with a first hydrophobic layer without CMC and a hydrophilic second one containing CMC. Electrochemical performances of the GDMs were tested in a single cell experiment; the active area was 23 cm², Nafion 212 membrane was used as electrolyte and the catalyst layer was coated directly onto the membrane. Hydrogen (0.2 NL/min) and air (1 NL/min) were used as the anodic and cathodic feedings, respectively.

The cell testing was run at two temperatures (60 °C and 80 °C) with different relative humidities (RH 80/100% and 80/60%, hydrogen/air). Electrochemical Impedance Spectroscopy (EIS) was carried out using a Frequency Response Analyzer. Impedance spectra were recorded (galvanostatic mode) at fifteen different current densities (CDs): from OCV to 1.3 A/cm². The experimental data were analyzed and fitted using an equivalent circuit model from Zview® software. Polarization and power density curves showed a better performance when the cell was assembled with double layer GDMs (Figure 1) which were able to manage water production in high current densities conditions, while single layer GDMs based cell showed a sudden drop of voltage. In particular, the best results were obtained at low relative humidities of inlet gases because CMC containing layers acts as water reservoir and keeps electrolytic membrane humidified and therefore proton conductivity as high as suitable for H⁺ mobility. However, electrochemical impedance spectroscopy (EIS) evidenced high mass transfer resistances which increase upon increasing CMC concentration, pointing out a non-optimal water management for such structured



1. Polarization and power density curves of fuel cells assembled with standard MPL (CMC-0) and with CMC-containing MPLs, at different concentrations of CMC. Operating condition: T=60 °C, RH=80-60% (anode-cathode)



2. Trends of Rd (diffusion resistance) as a function of current density for fuel cells assembled with GDMs based on innovative fluorinated polymers. For the sake of comparison, results with PTFE-based samples are also reported.

layers, in particular when relative humidity was high. Moreover, in a stand-alone study, carbon black powder was partially substituted by carbon nanotubes (CNTs) in the initial standard PTFE-based formulation. The rheological behaviour of inks and GDMs hydrophobicity (contact angle of 149°) were kept, but the presence of CNTs allowed higher power densities and lower ohmic resistances of the whole system, because of their higher conductivity with respect to carbon black one. The second part of the thesis dealt with the development of inks and coatings based on innovative, for the PEM fuel cells field, fluorinated polymers such as perfluoropolyether (PFPE), fluorinated ethylene propylene (FEP), perfluoroalkoxy (PFA) in order to substitute PTFE aiming to improve hydrophobic properties of final GDMs and consequently the water management during the fuel cell running. Such fluoropolymers

allowed to decrease considerably (from 305 °C down to 150 °C) the treatment temperature with respect to the one necessary with conventional PTFE-based MPLs (350 °C). All the novel polymers-based MPLs were found superhydrophobic, showing static contact angles higher than 150° (for PTFE-based samples, contact angle is around 145°). The performances of the cells assembled with the new GDMs, especially with FEP, were better than those obtained with traditional GDMs, in terms of maximum power density reached and water management since mass transfer resistance, related to diffusion limitations, were very low (Figure 2). In the last part of the work, the benefits introduced by FEP and by CNTs were combined. Thus, inks containing both of them were prepared, keeping polymer concentration fixed and varying CNTs concentration (from 1 % wt up to 10 % wt with respect to carbon black), in order to assess influence of

CNTs amount on final materials performances. GDM containing 10 % wt CNTs showed the best results in terms of global cell efficiency and maximum output power density. Durability of such a GDM, which is still a critical issue to be faced in fuel cells field, was evaluated. Both chemical and mechanical ad-hoc Accelerated Stress Tests (ASTs) were developed. They showed that the main degradation mechanism for GDM is due to mechanical stresses, caused by gases flow, which leads to erosion of materials, in particular surface carbon. In fact, part of microporous surface was lost and this caused a reduction of capability of managing water and a consequent dramatic mass transfer resistance increase. Whereas, chemical AST did not show substantial hydrophobic behaviour changes resulting in more restrained diffusion resistance increases. Thus, efficient GDMs were produced, even if some work for improving durability is still needed, in particular in terms of mechanical resistance, while a satisfying chemical resistance was obtained.

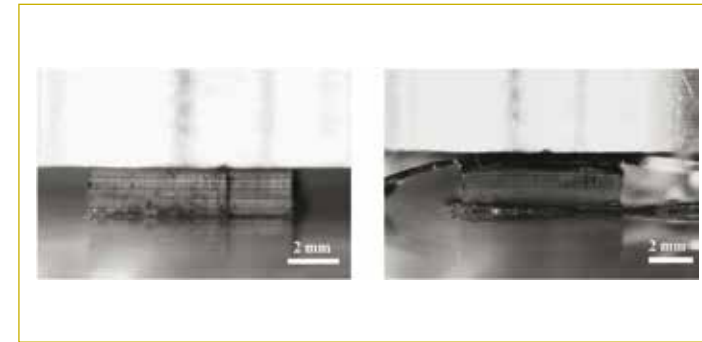
STRUCTURE-PROPERTY RELATIONSHIP IN VERTICALLY ALIGNED CARBON NANOTUBE FOAMS

Ludovica Lattanzi - Supervisor: L. De Nardo

The study of structure–function relationship in material science represents the starting point for realizing synthetic materials with properties tuned to specific application-driven needs. For instance, the design of geometrical architectures at the micro-scale paved the way for the development of energy absorption materials in applications where stringent limitations in weight and dimension are mandatory, e.g. space and transports. The best example of the fundamental role of structure–property relationship is represented by biological systems, where the excellent and multiple properties are strictly related to the highly organized nano- and micrometer scale architectures. Due to their excellent properties and high aspect ratio, carbon nanotubes (CNTs) have been proposed for several applications, including electrodes, batteries, supercapacitors, sensors, composite materials, scaffolds and drug delivery systems. Although most CNT commercialization today concerns the bulk applications, in which CNTs are incorporated or dispersed in other materials to create composite structures, there is a broad spectrum of research aimed to transfer these excellent properties

from nano- to macro-scale. Various macroscopic CNT-based materials have been fabricated. Examples include 1-D flexible yarns, 2-D sheets and 3-D vertically aligned CNT structures (VACNT forests/foams). Depending on the way they are assembled and fabricated, these structures exhibit different and fascinating properties. Among these, 3-D VACNT structures have a multi-scale fibrous organization, with features ranging from nanometer to millimeter scale, and graded functional properties. Vertical arrays of carbon nanotubes grown by the floating chemical vapor deposition method show unique mechanical behavior in compression, with a highly nonlinear response similar to that of open cell foams, the ability to recover large deformations, and unmatched energy absorption properties. The aim of the work consists in investigating the structure–property relationship in vertically aligned carbon nanotube (VACNT) forests in order to create structures with novel and improved properties. First we studied the bulk viscoelastic response of millimeter-long VACNT forests and we increased the complexity of the structure by embedding the forest between thin PDMS

layers and 2-D CNT macroscopic structure called bucky paper, to create a sandwich structure (Fig. 1). By using the mechanical design principles found in nature we introduced order at the micro-scale by synthesizing CNTs on substrates patterned with different growth templates: circles, lines, concentric rings (Fig. 2). We studied the effect of the micro-scale geometry on the quasi-static and dynamic mechanical responses of VACNT structures. Finally, inspired by the organic-inorganic composite materials found in nature and by the concept of “mechanical properties amplification”, i.e., materials with poor macro-scale mechanical properties can achieve orders-of-magnitude increases in strength and toughness, we deposited inorganic (calcium phosphate) and organic (chitosan) materials on patterned and non-patterned CNT structures and we studied their effect on the mechanical response. The patterned and non-patterned VACNTs were grown on silicon wafers by floating catalyst chemical vapor deposition. The micro-patterned CNT samples were grown on photolithographically silicon wafers. For the deposition of organic and inorganic materials we used the electrochemical deposition technique.



1. Optical images of (left) freestanding and (right) double-anchored VACNT forests.



2. SEM images of micro-structured VACNT forests: (top) concentric rings, (bottom-left) pillars and (bottom-right) lines.

The CNT structures were tested in quasi-static compression using an Instron E3000, and in dynamic using an impact test set-up. A high-speed camera coupled to a microscopic lens (Infinity) was used for in-situ visualization of the micro-scale dynamic deformation during the impact.

Nonlinear viscoelasticity of freestanding and polymer-anchored vertically aligned carbon nanotube foams: the bulk viscoelastic response of millimeter-long VACNT forests, both as freestanding material and in sandwich structure, was characterized using stress-relaxation and creep tests. To study the dependence of relaxation/creep rate on strain/stress levels, power functions of time were used to fit the stress-relaxation and creep curves. The stress-relaxation and creep tests performed on VACNT forests and sandwich structures showed a viscoelastic response. The trend of the power-law exponents suggested that freestanding and anchored CNTs followed a nonlinear viscoelastic response. The polymer on the top and bottom surfaces

of the samples affected the buckling mode and the stability of the material. Anchored CNTs presented higher stability (for moderate strain) than freestanding CNTs. The results supported the use of bulk CNT-based structures as building blocks for high strength, low-density energy absorption materials.

Geometry induced mechanical properties of carbon nanotube foams: the studies performed on micro-patterned CNTs showed the fundamental role of the pattern geometry on the mechanical response (energy absorption, peak stress, recovery of deformation) of VACNT structures. By changing the microstructural organization of VACNTs we fabricated lighter structures maintaining the mechanical response of non-patterned CNT structures (forests). The results showed the possibility to improve the efficiency of the structures as impact absorbers by controlling the micro-pattern geometry. *Organic-inorganic coated VACNTs:* the quasi-static and dynamic investigation on the hybrid organic-inorganic CNT

structures showed increase in stiffness and toughness with the deposition of chitosan and Ca-P. For example, at high impact velocity, the Ca-P coated VACNTs exhibited a ~8 times higher stiffness and a ~7 times higher energy absorption capability than the non-coated VACNTs. By changing the electrochemical deposition parameters and the geometry of the patterns we were able to tune the mechanical properties of VACNT structures. In summary, the manipulation of structure–property relationship in VACNT structures by acting on both large (millimeter) and small (micrometer) material architects allowed us to create light-weight and strong structural materials with enhanced energy absorption capability and shock response.

RESEARCH, DEVELOPMENT AND CHARACTERIZATION OF NOVEL, ADVANCED MOLYBDENUM-BASED COMPOSITES FOR LHC COLLIMATORS

Nicola Mariani - Supervisor: Ing. A. Bertarelli

Newly introduced particle accelerators such as the Large Hadron Collider (LHC) of CERN (Geneva, CH) feature a very large increase in the energy and energy density of the particle beams with respect to previous machines, bringing about the need for more efficient, reliable and robust Collimation Systems. These are designed to absorb stray particles before they heat superconducting magnets, inducing unwanted transitions from superconducting to normal conducting regimes (beam cleaning) and to protect the rest of the accelerator in case the beam orbit errors, intercepting the beam before it catastrophically impacts on delicate and expensive components (machine protection). The research of new materials for Beam Intercepting Devices (BID) is therefore receiving great impulse at CERN and in the rest of the particle accelerator's community with the aim to improve the cleaning efficiency and the robustness of BID.

In that framework, the aim of the present PhD work is to contribute to develop, characterize and produce new composite materials to be used in the near future for the active part (the so-called jaw) of the LHC Collimators. These materials must satisfy multiple requirements as to density

and average atomic number (cleaning efficiency), electrical conductivity (Radio-Frequency impedance), mechanical strength (Impact Resistance), thermal conductivity and thermal expansion (thermal stability). In addition, since such materials are heavily irradiated during their life cycle, it must not contain elements that create dangerous isotopes and must be able to withstand high cumulated doses before losing their properties by radiation-induced degradation. The thesis work has been divided into two main multi-disciplinary axes that are strongly interconnected between them: research and development of novel composites and their characterization in standard conditions and the experimental testing of proposed materials against a real proton beam impact, supported by real-time measurements and post-impact analysis.

The first part included a preliminary study of present solutions and available composites, the characterization of already developed materials like Copper Diamond (Cu-CD) and finally the research, development and characterization of new Molybdenum based composites. CuCD is a metal matrix composite produced by rapid Hot Pressing of Copper, Boron and Diamond powders

especially conceived for thermal management applications, developed by RHP Technology, Seibersdorf, Austria. The combination of the good physical properties of diamonds (high thermal conductivity, low thermal expansion and density) with the electrical conductivity of Copper give rise to a material having a Thermal Conductivity ~25% higher than Copper OFE with a Thermal Expansion Coefficient at RT of only 7 ppm/K. Unfortunately, the intrinsic brittleness of such material combined with its thermal instability at higher temperatures are somehow limiting the material appealing, so that a second R&D program has been launched to explore alternative composite families with higher thermal stability at high temperature.

The R&D of Molybdenum-based composites has been carried out in collaboration with BrevettiBizz Srl (Verona, IT) with the direct implication of the student who provided proposals for compositions and production cycles, microstructural, thermal and mechanical characterization and interpretation of results. The supporting thermo-mechanical characterization has been made under standard conditions using ad-hoc experimental apparatus that in certain cases has been designed and produced inside CERN EN/MME with the

contribution of the student, like the Thermal Conductivity (and Conductance) measuring apparatus described in the thesis work.

Molybdenum has been chosen as the main element because of its extraordinary mechanical properties combined with very high thermal stability and a good chemical affinity with carbon materials like Diamond and Graphite.

The most important milestones in the materials R&D presented in the thesis work are, in chronological order, Molybdenum Copper Diamond (MoCuCD), Molybdenum Carbide Graphite (MoGR) and Molybdenum Carbide Graphite Carbon Fibres (MoGRCF). MoCuCD has been a great improvement of CuCD from the mechanical point of view (thanks to the formation of Molybdenum carbides at the interface between diamonds and Molybdenum) but the presence of Copper used to fill the interstitials is still limiting its resistance to high Temperatures. On the other hand MoGR relies on the high Temperature reaction between Molybdenum and Graphite to promote the complete transformation of Molybdenum in refractory carbide Mo2C. One peculiarity of Mo2C is its metal-like electrical conductivity that results in a conductive MoGR

composite. In addition MoGR is completely refractory (TM>2500oC) and has a very high thermal stability, although its physical and mechanical properties are not exceptional. MoGRCF, finally, includes the refractory behaviour of MoGR while enhancing its Thermal and Physical properties by the addition of Carbon Fibres. The material is then sintered in Liquid Phase to melt and squeeze the interstitials between Fibres. The result is an outstanding material with a thermal conductivity in excess of 700 W/mK and a Density of only 2.8 g/cm³.

The second part of the thesis is the final testing of proposed materials against a direct beam impact to compare the different collimator materials in a real-life accidental situation. FEM analysis of the beam impact have been performed to predict the damage entity on standard collimator related materials. The simulations have been carried out using the commercial code Autodyn involving non-linear materials models like Equations Of State and complex Strength and Failure Models. The simulations allowed to predict (for known materials) the physical effective damage on the materials impacted by the proton beams and to properly tune the design of the samples and the sample holder

in order to obtain measurable parameters with the proposed experimental apparatus. The experiment, id. HRMT-14, took place into the HiRadMat facility at CERN (High Radiation to Materials) during September-October 2012, entailing the controlled impact on 6 different Collimator materials with increasing proton beam intensities of the Super Proton Synchrotron particles accelerator of CERN (operating at 440 GeV with a maximum intensity per shot of ~1014p). The energy deposited on the samples was enough to observe their explosion by a remotely controlled high speed video camera (during the High Intensity Shots). The video camera acquisition system development included the study of high speed imaging, the design of the acquisition layout (mirrors, lenses, samples position), the direct creation and usage of a home-made, radiation hard and synchronized lighting system and, finally, the interpretation of results. Finally, the proposed comparison of the different materials will be the background for the final choice of the LHC Collimator materials to be taken in next years at CERN.

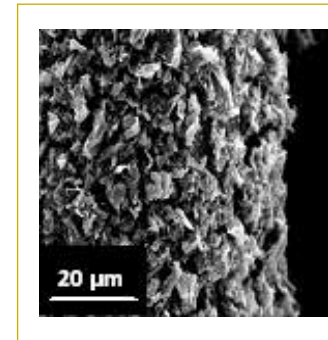
SYNTHESIS AND CHARACTERIZATION OF NANOMATERIALS FOR DATA STORAGE AND ENERGY STORAGE

Daniele Perego - Supervisor: S. Franz

The thesis is divided into three chapters, each dealing with different materials and devices. The first chapter is devoted to the study of materials and processes with impact in the field of energy storage. In particular graphene and its applications in the fabrication of electrodes for supercapacitors were investigated. Recent years has witnessed considerable concerns in terms of climatic changes and rising depletion of fossil fuel, thus resulting in much concentration on the investigation and development of the alternative and renewable resources. Compared with other sustainable resources, i.e. sun, wind, water and etc., electrical energy storage systems have played a larger role in our daily lives due to their availability on demand. The synthesis of graphene was carried out by chemical oxidation of Highly Oriented Pyrolytic Graphite (HOPG) powder (average size ~ 20 μm) followed by thermal and chemical reduction. Graphene oxide (GO) was prepared with the modified Hummers method. Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) analysis revealed that single graphene oxide layers were obtained, about $2 \times 3 \mu\text{m}$ wide and 1 nm thick. Pristine graphene was obtained by thermal reduction of GO in a controlled reducing atmosphere (H_2) at 450 $^\circ\text{C}$ for

2 h. TGA and FTIR confirmed that the thermal reduction removed the carboxyl groups while X-Ray Diffraction (XRD) evidenced the typical inter-layer distance of single layer pristine graphene (0.37 nm). However, Raman characterization revealed that after thermal treatment reduction was not complete. Graphene and graphene oxide based electrodes for supercapacitors have been fabricated by electrophoresis deposition onto metallic substrates (Ti, Ni, Al), as shown in Figure 1. The electrodes were characterized by 500 charge/discharge cycles in order to test and verify their electrochemical performances in aqueous electrolyte (1M Na_2SO_4 and 6M KOH). Results show an average specific capacitance of about 167 F g^{-1} at room temperature and 10 mV s^{-1} . The second chapter is dedicated to Thin-solid film Li-ion microbattery synthesis. This part of the PhD program has been developed at Massachusetts Institute of Technology (Boston, USA). The huge of energy demand for portable devices such as PDA, mobile phone and laptop computer requires high capacity and light weight battery. Since last generation rechargeable batteries have low capacity and environmental problems, the scientists have developed innovative rechargeable batteries that does

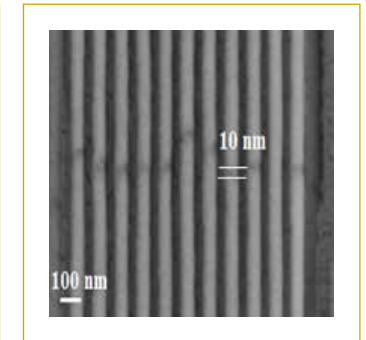
not have those disadvantages. Currently the conventional battery technologies, such as lead-acid and nickel cadmium, are being replaced by lithium-ion (Li-ion) batteries, fuel-cell technologies and nickel metal hydride batteries. Li-ion battery technology stands as a forerunner and market leader when compared to the other possible energy systems. In particular the work has been focused on the cathode active material as well as on the design and fabrication of a working thin-solid film Li-ion microbattery prototype. As cathode active material LiCoO_2 has been studied. LiCoO_2 thin films were deposited over a Si/ SiO_2 wafer by sputtering deposition and the relationship between its thickness, texture, electrochemical performances have been evaluated. In particular a transition is identified and located in correspondence of 1.12 μm thick LiCoO_2 thin film. Samples with higher thickness, after thermal annealing, present (104) PO, while samples with a thickness lower than 1.12 μm present (003) PO. Electrochemical tests show that PO affects not only the rate capability but even the electrochemical performance in terms of specific capacity. Finally (Figure 2) a working device has been designed, synthesized and characterized. The third and final chapter is



1. SEM micrograph of graphene based electrode for supercapacitor: a Ti current collector wire is covered by graphene which acts as active material in the energy storage process.



2. Top view image of two Thin-solid film Li-ion microbattery prototypes deposited over a Si/ SiO_2 wafer.



3. SEM cross-section of Au/10nm NiO/Au heterojunction nanowires embedded into AAO template.

dedicated to the synthesis and characterization of nanowires and their applications in the electronic field. In the electronic industry one of the major effort has always been devoted to the development of new memories increasing their speed and capacity. Modern semiconductor non-volatile memories, such as Flash memory, are successfully scaled down to achieve large storage capacity through the improvements in photolithographic technology. However, conventional scaling is expected to reach technical and physical limits in the next future. In order to overcome this problem, 'equivalent scaling', i.e. by introducing new materials and/or 3D nanostructures, has been proposed as alternative to the conventional scaling

technology. A wide range of non-volatile memory concepts has been proposed. In particular this part of the work has been focused on the electrochemical synthesis and characterization of metal/oxide/metal (MOM) nanowire (NW) heterostructures which show a peculiar electrical resistive switching behavior and could be used as building block for future high density non-volatile random access memory (ReRAM). MOM NW arrays were fabricated by electrodeposition of Au/Ni/Au multilayers into Anodic Aluminum Oxide (AAO) templates (pore diameter of 50 nm), followed by mechanical polishing of the AAO template and thermal oxidation (Figure 3). The electrodeposition of Ni and Au was carried out from sulphate-based and cyanide-

based electrolytes, respectively. Mechanical polishing of the resulting AAO templates was performed in order to expose the NWs from the AAO template surface, favoring thermal oxidation and allowing the electrical characterization of the NW array. Thermal treatments were carried out at 300 $^\circ\text{C}$ in air for 3 hours. Structure and morphology of the heterojunction NWs embedded into the AAO matrix were characterized by SEM, High Resolution Transmission Electron Microscopy (HRTEM), XRD and AFM. The resistive switching properties of the MOM heterojunction nanowires arrays were studied by current-voltage measurements using Scanning Probe Techniques (C-AFM).

SYNTHESIS OF NANOSTRUCTURED CARBON MATERIALS FOR ELECTROCHEMICAL ENERGY STORAGE

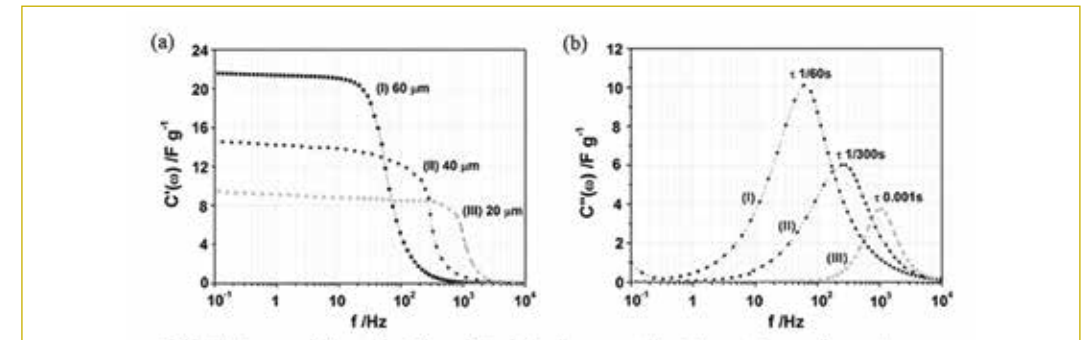
Fu Zhao - Supervisor: Antonello Vicenzo

In the search for novel energy storage solutions electrochemical capacitors (ECs) have risen to prominence as an important and rapidly growing class of devices. The last decade has witnessed an immense growth in research related to ECs. Current trends in the design of advanced ECs rely on novel electrode materials and nanostructures to reach higher performance level. Carbon nanotubes (CNTs) have gained wide popularity as a promising electrode material for next generation of ECs, due to their intrinsic properties and features, such as high electronic conductivity and electrochemical stability, low mass density, regular pore structures and highly accessible surface area. Hence, exploring novel fabrication routes for CNT-based electrodes so as to achieve enhanced power performance of ECs has become a research hot spot.

In this work, an industry scalable process for the fabrication of CNTs/Al electrodes for ECs has been developed, which includes the deposition of a Co-Mo catalyst film on Al foil by a wet chemical method and the direct growth of CNTs on Co-Mo coated Al by atmospheric pressure chemical vapor deposition. The process was designed so as to be readily amenable to a practical implementation, so that as-

grown CNTs/Al electrodes could be directly used for assembly of ECs without a subsequent treatment. In the first part of this work, with the aim of improving the CNT yield and also possibly tailoring the architecture of the CNT layer on Al, the focus was put primarily on the engineering of the catalyst film with enhanced catalytic activity towards CNT growth. Through the optimization of the catalyst preparation process, catalyst nanoparticles of distinct diameter and surface density were uniformly deposited on Al foils, making it possible to access to the diameter-controlled nanotube growth. Subsequently, the dependence of CNT growth kinetics on catalyst conditions (i.e. the catalyst particle size and distribution), and in turn the microstructure of resulting CNT mats, was investigated. The results show that CNT mats grown on the finest catalyst particles with a relatively low surface density on Al consisted of entangled fine nanotubes of diameter about 7 nm with a relatively high degree of the crystallinity of the CNT walls. With increasing the size and density of catalyst particles on Al, the resulting CNTs showed heterogeneity in diameter and a lower degree of the crystallinity of the CNT walls. Besides, it is also found that

the arrangement of nanotubes within the as-grown CNTs mat varied from the random entanglement to roughly vertical alignment with proceeding growth. Different CNT growth kinetics were discovered and discussed. Additionally, the growth time also showed a significant effect on the microstructure of as-grown CNT mats, i.e. an apparent increase in the population of finer CNTs and a concurrent shift towards aligned growth with extending the deposition period, which is caused by the fragmentation of the catalyst nanoparticles. In the second part of this work, the porosity of as-grown CNT mats was evaluated by performing nitrogen cryo-adsorption measurements. Two most important structural parameters - specific surface area, which is related to the charge storage or energy density of ECs, and the pore size that influences the electrolyte ion diffusion kinetics thus the power density of ECs- were obtained. The results show that the as-grown CNT mats possess a moderate specific surface area, and more importantly, a hierarchical pore structure consisting of both large mesopores and small micropores, which is a desired characteristic of the electrode materials for ECs. The microporosity (the ratio between



1. The frequency dispersion of the real (a) and imaginary part (b) of the complex capacitance of as-grown CNT ECs with different CNT layer thickness: 60 μm or type (I), 40 μm or type (II), and 20 μm or type (III)

micropores and mesopores) of as-grown CNT mats could be tuned easily by modifying the catalyst conditions for CNT growth, demonstrating the feasibility of tailoring the microstructure including the porosity of CNT-based electrodes by the proposed electrode fabrication method via CVD direct growth of CNTs on Al. In the last part of work, the electrochemical behaviors of as-grown CNT/Al electrodes and the correspondingly assembled ECs were thoroughly characterized. Basically, the ECs assembled using as-grown CNT/Al electrodes, namely, as-grown CNT ECs, exhibit an excellent power performance (with a maximum power density of 907 kW/kg), while the energy storage was limited due to the low yield of CNTs on Al

by CVD method. The specific capacitance of as-grown CNTs/Al electrodes increased from 18 to 83 F/g with varying the microstructure or thickness of CNT mats, counterbalanced by the decrease in the rate capability. Nonetheless, high rate capability, i.e. relaxation time constant within the millisecond range, was attained, thanks to the interconnected 3D network structure of the as-grown layer and the low contribution to the equivalent series resistance expected from the direct growth fabrication method. Furthermore, the as-grown CNT ECs showed good cyclability. Overall, this work has demonstrated that a simple catalytic CVD process for the direct growth of CNTs on Al foils can be an effective method to fabricate CNTs-based

electrodes for ECs, notably in the absence of special measures and processing steps finalized to a tight control of nanotubes growth and organization.