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# **General Information**

The EMN Dubrovnik Meeting on Porous Materials & Flexible Electronics will take place at Importanne Hotels & Resort, Dubrovnik, Croatia from October 21 to 25, 2019.

Workshops on various aspects related to Porous Materials & Flexible Electronics will include invited and contributed oral presentations from Tuesday to Wednesday, and the poster session will be presented on the afternoon of Wednesday.

## **Registration Desk Hours**

The meeting registration desk, located outside the meeting room **Coral**, will be open during the following hours:

Monday, October 21	15:00 -17:30
Tuesday, October 22	08:00 -18:00
Wednesday, October 23	08:00 -18:00

## **International Committees**

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# Meeting Program

<i>MON</i> Oct. 21		
(13:00-17:30PM)		
On Site Registration		
	<i>TUE</i> Oct. 22	
	Meeting Room: Cora	al
Session: FE I Chair: Xiaozhong Zhang		
9:00-9:25	A01: Inkjet-/3D-/4D-Printed Wireless Ultrabroadband Modules for IoT, SmartAg and Smart Cities Applications	<b>Manos M. Tentzeris</b> Georgia Institute of Technology, USA
9:25-9:50	A02: High mobility of amorphous oxide SiZnSnO thin film transistor for display applications	<b>Sang Yeol Lee</b> Cheongju University, Korea
9:50-10:15	A03: Flexible electronics with printed silicon	<b>Ryoichi Ishihara</b> Delft University of Technology, The Netherlands
10:15-10:30	Session E	Break
	Session: Porous Materials I Cha	air: David Faux
	A04: Gas physisorption for porosity	Tomáš Zelenka
10:30-10:55	characterization – some examples of misinterpretations	University of Ostrava, Czech Republic
10:55-11:20	A05: Porous materials for nanocatalytic carbon (di)oxide methanation	<b>Jaroslaw Polanski</b> University of Silesia, Poland
11:20-11:45	A06: Water Adsorption Mechanism on Porous Carbon Materilas	<b>Toshihide Horikawa</b> University of Tokushima, Japan
11:45-12:00	A07: Nitrogen and Fluorine Co-doped Activated Carbon for Supercapacitors	Juyeon Kim Energy Materials Center, Korea Institute of Ceramic Engineering & Technology, Korea

	A08: High-performance energy-storing	Xiong Pu
12:00-12:15	textiles enabled by nanostructured	Beijing Institute of Nanoenergy
	porous materials	and Nanosystems, CAS, China
12:15-14:00	Lunch B	reak

<i>TUE</i> Oct. 22 Meeting Room: Coral		
Session: Porous Materials II Chair: Tomáš Zelenka		
14:00 -14:25	A09: Small Holes in Graphene: a Key in Graphene-Assisted Chemical Etching of Semiconductor Surfaces	<b>Kenta Arima</b> Osaka University, Japan
14:25 -14:50	A10: Porosity of graphene synthesized using direct current plasma torch	<b>Ravil Amirov</b> Joint Institute for High Temperatures, RAS, Russia
14:50 -15:15	A11: Atomic-scale modeling of porous glassy systems and their surfaces towards the quantitative prediction of their structure and adsorption properties	Guido Ori Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), France
15:15 -15:40	A12: Nano-scale characterisation of porous material by fast-field-cycling NMR	<b>David Faux</b> University of Surrey, UK
15:40 -15:55	15:55 Session Break	
Session: FE II Chair: Manos M. Tentzeris		
15:55-16:20	A13: Scalable Fabrication of Energy Storage Systems for Printed and Flexible Devices	James Watkins University of Massachusetts, USA
16:20-16:45	A14: Solution-processed quantum dots for flexible optoelectronics	Iman S. Roqan King Abdullah University of Science and Technology, Kingdom of Saudia Arabia
16:45-17:10	A15: Fractal Architectures for Flexible Electronics: Laser Methods and Scalable Applications	Thanos Tiliakos National Institute for Laser, Plasma and Radiation Physics, Romania

17:10-17:35	A16: Spin Logic Device of In-memory Computing	<b>Xiaozhong Zhang</b> Tsinghua University, China
17:35-18:00	A17: Low-Dimensional Nanomaterials for Flexible Memory Devices	<b>Juqing Liu</b> Nanjing Tech University, China
18:00-18:15	A18: Polymeric foams for flexible and highly sensitive low-pressure capacitive sensors	<b>Mickaël Pruvost</b> MIE Lab - ESPCI, Paris, France
18:30PM	Dinner So	ocial

WED Oct. 23 Meeting Room: Coral		
Session: FE III Chair: Albert Cirera Hernandez		
9:00-9:25	A19: Inspection of structure by electromagnetic and vibration type actuator	<b>Hiroyuki Yaguchi</b> Tohoku Gakuin University, Japan
9:25-9:50	A20: Stretchable oxide electronics for sensing applications	<b>Madhu Bhaskaran</b> RMIT University, Melbourne, Australia
9:50-10:15	A21: Carbon Nanotube for Wearable and Robust Electronics	Kenji Hata National Institute of Advanced Industrial Science and Technology, Japan
10:15-10:40	A22: Oxide semiconductor based diodes, transistors, and circuits forwearable electronics	<b>Qian Xin</b> Shandong University, China
10:40-10:55	Session Break	
Session: Porous Materials III Chair: Mariem Kacem Boureau		
10:55 -11:20	A23: Rigid Plastic Models for Metallic Porous and Powder Materials	<b>Sergey Alexandrov</b> Beihang University, China
11:20-11:45	A24: Evolution for Iron(II) Spin Crossover Hofmann-like MOF Materials	<b>Takafumi Kitazawa</b> Toho University, Japan

11:45-12:10	A25: Li Diffusion in Garnet-type Electrolytes studied by the PFG NMR Spectroscopy	<b>Kikuko Hayamizu</b> University of Tsukuba, Japan
12:10-12:25	A26: Towards understanding gas flow in functionalized mesoporous membranes	<b>Benjamin Besser</b> University of Bremen, Germany
12:25-12:40	A27: Modelling the drying shrinkage of porous materials incorporating capillary and adsorption effects	<b>Ginger El Tabbal</b> EDF- Lab Paris-Saclay, France
12:40-14:00	Lunch Br	reak

WED Oct. 23 Meeting Room: Coral		
Session: Porous Materials IV Chair: Sergey Alexandrov		
14:00 -14:25	A28: Design of Porous Organic Salts (POS) with Versatile Function	<b>Norimitsu Tohnai</b> Osaka University, Japan
14:25 -14:50	A29: Discontinuous porosity approach to study a sand-clay media mixed with foam	Mariem Kacem Boureau Ecole Nationale d'Ingénieurs de Saint-Etienne, France
14:50 -15:15	A30: About Industrial Porous Materials: Limits of Pollutants Filtration within Carborundum Foam Ceramic Structures	Karim Ragui University of Sciences and Technology, Algeria
15:15-15:30	A31: Porosity characterization of wet solids: DSC thermoporometry and 1H NMR relaxometry	Vaclav Slovak University of Ostrava, Ostrava, Czech Republic
15:30-15:45	A32: A self-standing supercapacitor electrode based on MOF-derived NiO/C@CNF composite	<b>Seoyoon Shin</b> Yonsei University, Korea
15:45-16:20 POSTER SESSION Chair: Sergey Alexandrov		
Session: FE IV Chair: Madhu Bhaskaran		
16:20-16:45	A33: New Flexible Hybrid Electronics Technologies for Biomedical Application	<b>Takafumi Fukushima</b> Tohoku University, Japan

16:45-17:10	A34: Polymer Assisted Deposition of Epitaxial Oxides Thin-Films and Multilayers	José M. Vila-Fungueiriño Université de Montpellier, France; Universidade de Santiago de Compostela, Spain
17:10-17:35	A35: Hybridizing SMD technology with inkjet Printed Circuit Board	Albert Cirera Hernandez Universitat de Barcelona, Spain
17:35-18:00	A36: Novel Antennas and RF Structures for Wearable Technology and IoT Applications	Haider Raad Xavier University, USA
18:00-18:25	A37: Ultra-thin Langmuir–Blodgett thin films: Gas sensing and energy harvesting applications	Vibha Saxena Bhabha Atomic Research Centre, India
18:30	Dinner Social	
THU Oct. 24 (One-day Excursion)		

WED Oct. 23		
Poster session Chair: Sergey Alexandrov 15:45 -16:20		
P01: Optimization of oxygen chemisorption on the carbon surface based on kinetic analysis of isothermal thermogravimetry	<b>Gabriela Hotová</b> University of Ostrava, Czech Republic	
P02: Characterization of porous carbon paper electrode prepared from the bleached rice husk pulps for supercapacitor application	<b>Hye Kyoung Shin</b> Jeonju University, Korea	
P03: The effect of ILs as co-salts in electrolytes for high voltage supercapacitors	Kwang Chul Roh Energy Materials Center, Korea Institute of Ceramic Engineering & Technology, Korea	
P04: The effect of porosity on sorption properties of oxide materials	Agnieszka Martyla Łukasiewicz Research Network - Institute of Non-ferrous Metals Division in Poznan, Poland	

	Monika Osinska-Broniarz
P05: Porous organosilanes as potential sorbents of	Łukasiewicz Research Network -
hydrogen	Institute of Non-ferrous Metals
	Division in Poznan, Poland
P06: A study on a hybrid index matching layer of the	Guneik Jang
Mn SnO2/Ag/Mn SnO2 tri layer film on DET substrate	Chungbuk National University,
MII-SIIO2/Ag/MII-SIIO2 UI-layer IIIII on FET substrate	Korea
	Zanan Dadiyaiayia
P07: Wearable Piezo Haptic Matrix	Nalia Dall Lab Cambridge UK
	Nokia-Bell Lab, Cambridge, UK
	Jong-Hyun Lee
P08: Novel 2-Micrometer Ag-Coated Cu Materials for	Seoul National University of
High-Speed Die-Attach at below 250 °C	Science and Technology, Seoul,
	Republic of Korea
	M 1/
P09: Advanced nanostructured carbon/flexible polymer	Maris Knite
composites for multifunctional sensing	Riga Technical University, Latvia
	Jai-Won Byeon
P10: Effect of Mechanical Fatigue on Flexible Lithium	Seoul National University of
Ion Battery for Wearable Electronics Applications	Science and Technology, Seoul,
	Korea
P11: Effect of Mechanical Fatigue on the Functional	Jang-Hun Jo
Degradation of Flexible Transparent Conductive	Seoul National University of
Ag-nanowire Film	Science and Technology, Korea

# **Abstract Session**

# A01: Inkjet-/3D-/4D-Printed Wireless Ultrabroadband Modules for IoT, SmartAg and Smart Cities Applications

<u>Manos M. Tentzeris</u> Georgia Institute of Technology, USA Email: <u>etentze@ece.gatech.edu</u>

#### Abstract:

In this talk, inkjet-/3D-printed antennas, interconnects, "smart" encapsulation and packages, RF electronics, microfluidics and sensors fabricated on glass, PET, paper and other flexible substrates are introduced as a system-level solution for ultra-low-cost mass production of Millimeter-Wave Modules for Communication, Energy Harvesting and Sensing applications. Prof. Tentzeris will touch up the state-of-the-art area of fully-integrated printable broadband wireless modules covering characterization of 3D printed materials up to E-band, novel printable "ramp" interconnects and cavities for IC embedding as well as printable structures for self-diagnostic and anti-counterfeiting packages. The presented approach could potentially set the foundation for the truly convergent wireless sensor ad-hoc networks of the future with enhanced cognitive intelligence and "rugged" packaging. Prof. Tentzeris will discuss issues concerning the power sources of "near-perpetual" RF modules, including flexible miniaturized batteries as well as power-scavenging approaches involving thermal, EM, vibration and solar energy forms. The final step of the presentation will involve examples from shape-changing 4D-printed (origami) packages, reflectarrays and mmW wearable (e.g. biomonitoring) antennas and RF modules. Special attention will be paid on the integration of ultrabroadband (Gb/sec) inkjet-printed nanotechnology-based backscattering communication modules as well as miniaturized printable wireless (e.g.CNT) sensors for Internet of Things (IoT), 5G and smart agriculture/biomonitoring applications. It has to be noted that the talk will review and present challenges for inkjet-printed organic active and nonlinear devices as well as future directions in the area of environmentally-friendly ("green") RF electronics and "smart-skin' conformal sensors.

# A02: High mobility of amorphous oxide SiZnSnO thin film transistor for display applications

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High-performance thin-film transistors were fabricated with simply changing various device parameter. Amorphous SiZnSnO TFT was confirmed to have high stability as well as high mobility. This could be achieved by suppressing the oxygen vacancies through the strong bonding strength with the oxygen of Si atoms. [1,2]

Furthermore, we analyzed the electrical characteristics and stability with various parameters using the capping structure. Figure 1 shows the electrical characteristics varied depending on the work function and resistance of the capping layer. This can be explained by two mechanisms: i) the injection or depletion of electrons by the capping layer. ii) current path is formed in the  $\omega$ -shape by the intermediate capping layer. [3] In addition, a systematic change in capping length provides better characteristics by decreasing the influence of the interface between gate dielectric and active channel layer, as well as more electron injection. It can be directly applied to next-generation display applications.



- Fig1. Energy band diagram of AOS-TFTs with different capping layer (a) non-contact. (b) Electron injection model (when  $\Phi_{AOS} > \Phi_{capping layer}$ ). (c) electron depletion model (when  $\Phi_{AOS} < \Phi_{capping layer}$ ).
- B. H. Lee, D-Y. Lee, A. Sohn, S. Park, D-W. Kim, and S. Y. Lee, J. Alloy. Compd. 715, 9-15 (2017).
- 2. J. Y. Choi, K. Heo, K-S. Cho, S. W. Hwang, S. Kim and S. Y. Lee, Sci. Rep. 6, 36504 (2016).
- 3. B. H. Lee, A. Sohn, S. Kim, and S. Y. Lee, Sci. Rep. 9, 886 (2019).

## A03: Flexible electronics with printed silicon <u>Ryoichi Ishihara</u> Delft University of Technology, The Netherlands

# A04: Gas physisorption for porosity characterization – some examples of misinterpretations

#### Tomáš Zelenka

Department of Chemistry, University of Ostrava, Ostrava, Czech Republic Email:tomas.zelenka@osu.cz

Gas physisorption method is one of the most widely used tools for the textural characterization of micro- and meso-porous materials. Despite both, the commercial availability of hi-tech gas physisorption instruments and software for evaluation of sorption isotherms, a correct interpretation of results may still be problematic.

The contribution focuses on an overview of some models/approaches used for evaluation of physisorption isotherms and subsequent misinterpretations that may occur. For example, the BET model, although published more than 80 years ago, is still widely used to evaluate the surface area of materials. When the material is microporous, one has to be careful when applying the BET model and interpreting results.

In the case of pore size distribution, the results may vary considerably depending on whether the adsorption or desorption branch of the isotherm is selected for calculations. The problem may arise when the hysteresis loop is of type H2 (according to IUPAC 2015 [1]). This one is typical for complex pore structures such as a system of interconnected ink-bottle pores (wide pore bodies interconnected by narrow pore necks), where pore blocking and

cavitation belonging to the network effects, play a significant role. Using the appropriate branch should not never be straightforward for calculation of pore size distribution. When the desorption of adsorbate is controlled by the pore blocking mechanism, the desorption branch can provide valuable information about neck size distribution. On the other hand, in the case of the cavitation mechanism, no quantitative information about neck size distribution can be obtained. Information about pore body size distribution can still be obtained from the adsorption branch.

A similar issue may arise during the interpretation of results from H3, H4, and H5 types of hysteresis loops that are characteristic for their sharp step-down on the desorption branch at about 0.4 - 0.5 of relative pressure (for N<sub>2</sub>/77K) [1]. The pore size distribution calculated from the desorption branch (e.g. by conventional BJH model) then gives an artifact on pore size distribution at about 3.5 - 4.5 nm of pore diameter [2] which may also lead to misinterpretation.

- 1. M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K. S. W. Sing, *Pure and Applied Chemistry* **87**, 1051 (2015).
- 2. T. Zelenka, Microporous and Mesoporous Materials 227, 202 (2016).

#### A05: Porous materials for nanocatalytic carbon (di)oxide methanation

#### Jaroslaw Polanski

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Carbon is a crucial element for human life. Although it supports our life, excess carbon dioxide has been recognized as an important pollutant that endangers human existence. One concept for the sustainable management of carbon dioxide involves its use as a potential source of the carbon for chemical industry.  $CO_2$  could be an attractive, renewable, safe and inexpensive  $C_1$  building block for both organic chemistry and fuel engineering. For example, the catalytic photothermal version of  $CO_2$  methanation – can potentially be used to produce solar fuel [1]. Water/carbon dioxide splitting could yield solar syngas (H<sub>2</sub> + CO) [2-4], and the methanation of solar CO or syngas (a blend of H<sub>2</sub> and CO) yields a synthetic replacement for natural gas. However, the progress of sustainable chemistry for carbon (di)oxide methanation requires the development of novel catalytic materials in order to make the process economically profitable. Low-temperature processing is one option here

[5]. During the lecture we will discuss the recent concepts and developments in this area extensively.

We recently described nanocatalysts that were constructed of nanometalic particles that had been created using nanoporous silica for low-temperature chemistry [6-8]. During the lecture, we will discuss the application of novel materials that were created as efficient catalysts of low-temperature ammonia cracking, Sonogashira coupling, glycerol oxidation or dehydration and DeNOx. Processing CO<sub>2</sub> and CO will be especially discussed during the lecture, e.g. Ni-supported Ru nanoparticles in silica [5]. Figure 1 shows the catalyst system. The method for supporting Ru nanoparticles on Ni included the formation of nano-Ru/nano-SiO2 from which nanoporous silica was digested in the presence of Ni. This provided a nano-Ru/Ni catalyst with an oxide passivation layer on the surface in which unalloyed metallic Ru and Ni were detected. This system, which was tested as a potential methanation catalyst, appears to be highly productive and efficient at low temperatures, e.g. ca. a 100% conversion can be achieved at ca. 200°C at a high TOF value of 940 h–1. In turn, the highest methane productivity (among nano-Re, Rh, Ir or Pd/Ni) obtained at a TOF value of ca. 13855 h–1at a higher temperature (460°C) was observed for the nano-Re/Ni catalyst.



Fig1. Structure of silica-supported Ru NPs in a 1.5% Ru/Ni catalyst [6].

- 1. X. Meng, et al., Angew. Chem. 126, 11662 (2014).
- 2. Ch. Agrafiotis, et al. Renew. Sust. Energ. Rev. 42, 254 (2015).
- 3. W.C. Chueh, et al. Science 330, 1797 (2010).
- 4. D. Marxer, et al. Energy Environ. Sci. 10, 1142 (2017).
- 5. Y. Yuqiang, et al. Int J Hydrogen Energy 43, 23201 (2018).
- 6. J. Polanski, et al., Applied Catalysis B: Environmental 206, 16 (2017).

- 7. M. Kapkowski, et al. and J. Polanski *Applied Catalysis B: Environmental* 202, 335 (2017).
- 8. M. Kapkowski, et al. and J. Polanski *Applied Catalysis B: Environmental* 239, 154 (2018).

#### A06: Water Adsorption Mechanism on Porous Carbon Materials

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Adsorption isotherms of water on porous carbons, such as activated carbon, exhibit very large hysteresis loops. It is now believed that the origin of the hysteresis in water adsorption is different from that of adsorption of simple gases in mesoporous solids, where the difference in the curvature of the interface separating the adsorbed phase and the gas phase is the principal reason for the hysteresis. In this presentation, we present the differences of water adsorption isotherms on graphitized carbon black (flat surface), micropores, and mesopores (shown in Fig. 1), and discuss in details the mechanisms of water adsorption on these materials by analyzing the descending scanning curves. For flat surfaces and misoporous solids, although hysteresis loops are observed the behavior of the hysteresis is different. For the flat surface, the loop extends over a very wide range of pressure and it is greater when descending is started at higher loadings; on the other hand, for the mesoporous carbon the hysteresis loop shows three distinct steps. For microporous carbon, the hysteresis is observed over a narrower range of reduced pressure than that for flat surfaces. By analyzing the desorption scanning curves from different loadings and the isosteric heat, we put forward the following mechanism for water adsorption: (1) water molecules adsorbing on functional groups located at the junctions between adjacent basal planes of graphene layers, (2) growth of water clusters around the functional groups, and (3) bridging of adjacent clusters to form condensate which eventually fill the confined space, and the extent of this pore filling depends on the size of the confined space [1-4].

We will also demonstrate the water adsorption isotherms on carbon materials which have a broad pore size distribution spanning from micropores to mesopores. One sample has a distinct micropore distribution from the mesopore distribution, while the other sample has continuous



pore size distribution from micropore to mesopore [5, 6].

Fig. 1 Water adsorption isotherms at 298 K on flat surface, microporous and mesoporous carbons

References:

[1] <u>T. Horikawa</u>, et al., *Carbon* **95**, 137-143, 2015.
 [2] <u>T. Horikawa</u>, et al., *Aus J Chem* **68**, 1336-1341, 2015.
 [3] <u>T. Horikawa</u>, et al., *J Colloid Interf Sci* **439**, 1-6, 2015.
 [4] <u>T. Horikawa</u>, et al., *Carbon* **124**, 271-280, 2017
 [5] <u>T. Horikawa</u>, et al., *Carbon* **49**, 416-424, 2011.
 [6] <u>T. Horikawa</u>, et al., *Carbon* **56**, 183-192, 2013.

### A07: Nitrogen and Fluorine Co-doped Activated Carbon for Supercapacitors

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Activated carbon has a lower electrical conductivity and reliability than other carbonaceous materials because of its oxygen functional groups that are formed during the

activation process. This problem can be overcome by doping with heteroatoms to reduce the number of oxygen functional groups. In the present study, N, F co-doped activated carbon (AC-NF) was successfully prepared by a microwave-assisted hydrothermal method, utilizing commercial activated carbon (AC-R) as a precursor and ammonium tetrafluoroborate as a single source for N, F co-doping. AC-NF showed improved electrical conductivity (3.8 S cm<sup>-1</sup>) with N and F contents of 0.6 and 0.1 at%, respectively. The introduction of N and F improved the performance of supercapacitors: AC-NF exhibited improved rate capability at current densities of 0.5–50 mA cm<sup>-2</sup>. The rate capability was high compared to that of raw activated carbon because N, F co-doping increased the electrical conductivity of AC-NF. The developed N, F co-doping method using a single source is cost-effective and yields AC-NF with excellent electrochemical properties, making it a promising method for the commercialization of energy storage devices.

# A08: High-performance energy-storing textiles enabled by nanostructured porous materials

### Xiong Pu<sup>1,2</sup>

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#### <sup>2</sup>School of Nanoscience and Technology, University of Chinese Academy of Sciences, Beijing, China

Rapid advancements in wearable smart textiles impose the challenge on corresponding power devices that they should possess comparable flexibility, stretchability and functionalities. In this talk, we briefly summarize our recent progresses on wearable energy storage and harvesting devices, especially energies devices aiming to power smart textiles. Yarn- or textile-based electrochemical energy storage devices have been developed based on porous electrode materials. An energy-storing varn-type asymmetric supercapacitors (Y-ASC) is reported. Common polyester yarns with conformal Ni/Cu coating are utilized as 1D current collectors in Y-ASCs. The solid-state Y-ASC achieves high areal energy density ( $\approx 78.1 \ \mu\text{Wh cm}^{-2}$ ), high power density (14 mW cm<sup>-2</sup>), stable cycling performance (82.7% for 5000 cycles), and excellent flexibility (1000 cycles bending for 180°). Furthermore, a rechargeable textile alkaline Zn microbattery (micro-AZB) fabricated by a process analogous to traditional resist-dyeing Conductive realized by techniques. patterned electrodes are first resist-aided electroless/electrodeposition of Ni/Cu films. The resulting coplanar micro-AZB in a single textile, with an electroplated Zn anode and a  $Ni_{0.7}Co_{0.3}OOH$  cathode, achieves high energy

density (256.2 Wh kg<sup>-1</sup>), high power density (10.3 kW kg<sup>-1</sup>), and stable cycling performances (82.7% for 1500 cycles). The solid-state micro-AZB also shows excellent mechanical reliability (bending, twisting, tailoring, etc.). Our work provides new opportunities for soft power sources and potential applications in electronic textiles.



Fig1. Resist-dyed textile aqueous Zn microbatteries.

- M. Liu, X. Pu, Z. Cong, Z. Liu, T. Liu, Y. Chen, J. Fu, W. Hu, Z. L. Wang, ACS Appl. Mater. Interfaces 11, 5095 (2019).
- M. Liu, Z. Cong, X. Pu, W. Guo, T. Liu, M. Li, Y. Zhang, W. Hu, Z. L. Wang, Adv. Funct. Mater. 1806298 (2019).

# A09: Small Holes in Graphene: a Key in Graphene-Assisted Chemical Etching of Semiconductor Surfaces

#### Kenta Arima

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Metal-assisted chemical etching is a simple and low-cost etching process for semiconductor surfaces [1]. There have been many reports on this etching mode of Si surfaces loaded with noble metals in HF solutions with oxidants such as  $H_2O_2$ . We have applied this etching mode to the machining of a Ge surface, such as patterning [2] and flattening [3], by the catalytic activity of Pt or Ag in O<sub>2</sub>-containing water. However, a problem with this system is the use of noble metals as catalysts. After metal-assisted chemical etching, residual metals on the semiconductor surface have to be removed. For example, aqua regia is effective for

dissolving Pt. However, such a strong oxidative solution causes severe damage to a Ge surface. To solve this issue, graphene can be used as a substitute for noble metals to achieve catalyst-assisted chemical etching. An advantage of graphene over metallic catalysts is that, unlike metals, oxygen plasma is effective for removing graphene on a solid surface. Another has reported graphene-assisted chemical etching of Si with group chemical-vapor-deposition-grown graphene as a catalyst [4]. Recently, we reduced a commercial graphene oxide (GO) solution by hydrazine monohydrate to obtain a black suspension including reduced GO (rGO) sheets. Then we dispersed single sheets of rGO on a Ge surface by simple spin coating, and immersed the sample in water with dissolved O<sub>2</sub> molecules. As shown in Fig. 1, we demonstrated enhanced chemical etching of Ge surfaces under the sheets [5].

According to literature [6], it is believed that an rGO sheet has small holes of size smaller than 5 nm<sup>2</sup>, of which area percentage is 2%. In the rGO-assisted chemical etching, such small holes, as depicted in Fig. 2(a), play an important role. Figures 2(b)-2(e) show the reaction sequence of this etching [7]. As shown in Fig. 2(b), the edges of small holes in rGO promote the dissociative adsorption of O<sub>2</sub> molecules to oxidize a Ge surface underneath. The resultant GeO<sub>2</sub> dissolves in water promptly, which is followed by the formation of an etched hollow as shown in Fig. 2(d). At present, however, there remain two problems. One is a roughened morphology at the etched hollows, as illustrated in Fig. 2(e). The other is a low etching rate of only several nm/h at water temperature of 23°C. Our strategy is to solve both problems by increasing the density of small holes in an rGO sheet. I will present our recent challenges to form a porous graphene catalyst for a better performance of graphene-assisted chemical etching.

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#### A10: Porosity of Graphene Synthesized Using Direct Current Plasma Torch

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Experimental studies of the synthesis of graphene in a plasma jet reactor based on a direct current plasma torch with an expanding anode channel with an electric power of up to 40 kW have been carried out [1,2]. Helium, argon and nitrogen were used as plasma-forming gas at pressures of 150-730 Torr. Methane, propane-butane mixture and acetylene were used as carbon precursors. The obtained graphene materials were investigated by scanning and transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, thermogravimetry and Raman spectroscopy. To determine the characteristics of the porous structure (pore volume, pore radius, surface area) a relatively new method of adsorption "Limited Evaporation" [3] based on the analysis of the kinetics of evaporation of the adsorbate from the test material was used.

It was shown that by using plasma jet multi-layered graphene materials may be formed without the presence of catalysts. Morphology and structural properties of the materials depend on carbon source, flow rate and the gas pressure. These materials are composed of polycrystalline graphene flakes with a highly developed porous structure formed mainly of macro- and mesopores with different diameters. The total volume and area pore depending on their radius have been found. These results showed that the synthesized carbon structures using the plasma jet are mesoporous. The correlation between the conditions of synthesis and specific surface area of graphene materials has been determined.

The possibility of direct hydrogenation of graphene materials during their synthesis and the production of graphane was discovered. The N-doped graphene synthesis in a nitrogen plasma jet has been studied. Photoelectron spectroscopy has shown that in the N-graphene synthesized pyridine nitrogen, which is not an electron donor, predominated. Graphene structures containing copper during acetylene conversion using plasma jets of nitrogen and helium were obtained. The presence of copper does not change the morphology of the synthesized products. Increasing the power of the plasma torch increases the copper content in the structures of graphene materials due the erosion of the anode of plasma torch.

As a result of numerical simulation, the kinetic mechanism of the formation of carbon phase precursors in the gas phase, namely,  $C_2$  dimers, was studied for helium/propane-butane plasma. The concentration of  $C_2$  was determined depending on the temperature and compared with the literature data on the pressure of saturated carbon vapors in the temperature range of 2500-5000K. It is shown that the  $C_2H$  involving reactions provide additional  $C_2$  production leading to the formation of supersaturated vapor from C2 molecules in the temperature range of 2500-3500 K.

Porous graphene materials have been used in various applications. The effect of nitrogen-containing graphene on the structure of the water-repellent agent and the activity of gas diffusion cathodes for air-metal fuel cells was investigated. It is found that the structure of the active layers of cathodes based on graphene differs from those based on activated carbon. The graphene materials were incorporated into the electrodes for the supercapacitor and effect of their additives on capacitive of the supercapacitor characteristics has been determined. The composite ceramics based on cubic boron nitride and graphene was synthesized. It is found that the average ultimate strength of ceramics reached a maximum when the graphene content was 0.5%

The authors gratefully acknowledge Russian Foundation for Basic Research for the support by Grant Nos. 18-08-00306 and 19-08-00081.

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# A11: Atomic-scale modeling of porous glassy systems and their surfaces towards the quantitative prediction of their structure and adsorption properties

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Owing to their large surface area and tunable pore size, amorphous porous solids such as siliceous, carbonaceous and chalcogenide materials are at the heart of important applications: heterogeneous catalysis, energy (H<sub>2</sub> storage, lithium batteries) and environment (water treatment, nuclear waste storage). Recently, nanoporous chalcogenides (chalcogels) have been demonstrated to be efficient sorbents for environmental remediation from gaseous and water waste media.<sup>[1-2]</sup> From a computational point of view, producing glassy surface models capable of mimicking realistically the behavior of a chalcogel and its surface is mandatory in order to understand the structure and adsorption properties of such complex amorphous materials. In this contribution, first-principles molecular dynamics (FPMD) within the framework of density functional theory (DFT) and grand canonical Monte Carlo (GCMC) simulations are combined to study the properties of glassy chalcogenide surfaces. Different pore sizes, chemical stoichiometries and compositions will be considered. FPMD is used to develop a realistic model of these materials with special emphasis on their surface chemistry.<sup>[3-5]</sup> A detailed account of the structure of the surface models is given in terms of pair correlation functions, structure factors, chemical order and chemical bonding. The surface properties of these materials will then be assessed by simulating adsorption isotherms of various fluids using GCMC simulations. I will show how the realistic details of the surface chemistry drastically affect the adsorption of various gases such as  $N_2$ ,  $CO_2$ ,  $CH_4$ , H<sub>2</sub> and their mixtures.<sup>[6,7]</sup>

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#### A12: Nano-scale characterisation of porous material by fast-field-cycling NMR

Fast-field-cycling nuclear-magnetic resonance (FFC-NMR) experimentation on porous material measures the relaxation rate  $T_1^{-1}(f)$  as a function of NMR frequency f over many orders of magnitude of f. The dispersion curves capture information about the nano-scale dynamics of proton bearing fluids in the porous material spanning timescales from picoseconds to microseconds - provided the curves can be fit to suitable model. The  $3\tau$  model [Phys. Rev. E., 95, 033116 & 033117 (2017)] can be fit to  $T_1^{-1}$  relaxation rate dispersion curves over the full frequency range for a wide range of porous material, including mortar, clay, plaster and rock. Fits yield three characteristic diffusion time constants plus estimates of the characteristic pore dimension. Their relationship to surface affinity is discussed. Finally, it is shown that FFC-NMR can, in principle, distinguish between fluid in closed, channel and planar pores.

#### A13: Scalable Fabrication of Energy Storage Systems for Printed and Flexible Devices

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The miniaturization of printed and flexible devices, including autonomous intelligent sensor platforms for IOT and human health applications, is driving a parallel need for highly efficient energy storage systems that are inexpensive to produce, exhibit high power and energy densities, and occupy a minimum footprint on the device. Microbatteries and supercapacitors based on 3D architectures hold great potential to meet these demands, but haven proven difficult to fabricate using scalable approaches suitable for large scale production. Reports of high-performance, fully integrated 3D microbatteries in particular are quite limited.

We are examining the production of nanostructured energy storage devices using nanoimprint lithography1,2, self-assembly3, and in some cases novel approaches to materials processing. In one example, 3D lithium-ion microbatteries are fabricated via imprint lithography using inks comprised of sub-10 nm LiMn2O4 and Li4Ti5O12 nanoparticles and the battery cell is integrated vertically through layer-by-layer (LBL)

assembly.1 The batteries are shown to possess superior capacity retention (40% at 300 C) and high-power density (855.5 (855.5  $\mu$ Wcm-2 $\mu$ m-1)) comparable to some of the best microsupercapacitors. We further show that it is possible to fabricate true 3-D woodpile battery anodes using imprint lithography wherein the areal capacity scales directly with the number of layers2 and to prepare conformal polymer separators on complex electrode architectures using initiated chemical vapor deposition4. Finally we demonstrate the fabrication of hierarchical multi-layer graphene/carbon/FeOx nanoparticle composite anodes for Li ion batteries using a combination of imprint lithography and photothermal processing. The approach is rapid and highly efficient, enabling batch fabrication strategies for microbattery systems as well as the roll-to-roll production of large energy storage batteries.

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### A14: Solution-processed quantum dots for flexible optoelectronics

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Wide and direct bandgap semiconductors (WBSs) are promising materials for many deep UV (DUV) applications. However, several challenges presently hinder the enhancement of DUV optoelectronics, such as low crystal quality, as well as complex and costly fabrication and growth processes that prevent production of high-performance devices, especially for large-scale applications. Here, we reported in this presentation, we demonstrate several novel cost effective WBS-based devices based on solution processed quantum dots with improved or novel functionalities, for the first time. We used a simple solution based method using femtosecond-laser ablation in liquid (FLAL) to synthesize high-quality WBS quantum dots (QDs), such as ZnO, MnO and Ga2O3 QDs. Adoption of

this novel strategy allows producing highperformance self-powered solar-blind DUV photodetectors based on both Schottky and heterojunction structures that can be used for fixable devices. We show that the responsivity of solution-processed QDs based devices was improved to > 700 mA/W for Shottkey devices and reaches to up to  $\sim 300$  x103 mA/W for QDs/ -Ga2O3 nano-flake devices heterojunction. The devices were fabricated by simple drop-casting or spray-coating QDs on interdigitate metal electrode (IDE) on silicon oxide and flexible substrates.[1,2] The optical and structural characterizations reveal high QD quality. This work paved the way to introduce cost-effective and high performance devices for flexible large scale applications.



Figure 1: The simple FLAL method used for cost effective flexible devices. Drop-casting and spray-coating methods on spray-coated on IDE deposited on a silicon oxide substrate as well as flexible substrates to fabricate the device.

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# A15: Fractal Architectures for Flexible Electronics: Laser Methods and Scalable Applications

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New chapters in flexible electronics technology have been initiated by the adoption of revolutionary 2D materials and by developing targeted methods for their application. The latest research trends mandate the use of lasers to directly inscribe electrode designs onto flexible substrates via laser pyrolysis of polymeric precursors, or to drive the photopolymerization of precursor gels in 3D printing SLA applications. We investigate such methods by providing an informed overview of laser equipment, precursors, and end-products, and we elucidate on our own research on microelectronics, with applications in supercapacitors, fuel cells, and antennas [1,2]. We introduce novel fractal geometries for optimized planar electrodes by revamping past groundbreaking ideas, and we advocate for the intelligent use of auxiliary nonlinear metrics for both material characterization and form-factor optimization [2,3]. Finally, we address common pitfalls and misconceptions associated with lack of validation and the improper choice of characterization metrics, both stemming from the competitive dynamics plaguing the academic environment.



- Fig1. Laser scribing on polyimide substrates for flexible fractal supercapacitors (left), 2-photon polymerization by SLA 3D-printing for flexible fractal micro-antennas (right). Designs are based on the Space-Filling Carpet architecture.
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### A16: Spin Logic Device of In-memory Computing

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Coupling semiconductor nonlinear transport effect and Hall effect in semiconductor, we developed a Si-based geometrical enhanced MR device whose room-temperature MR ratio reaching 30% at 0.065 T [1-3]. We further coupled semiconductor nonlinear transport effect and anomalous Hall effect in a Perpendicular Magnetic Anisotropic (PMA) material, and realized a giant MR of 22000% at 1mT in PMA material at room temperature. Based on our Si based MR device, we developed a current-controlled reconfigurable MR logic device, which could perform all four basic Boolean logic including AND, OR, NAND and NOR in one device [4]. We proposed an alternative way to realize magnetic logic by coupling spin-dependent transport effect in magnetic material and nonlinear transport effect in semiconductor material [5]. We further proposed a non-volatile reconfigurable spin logic-memory device by coupling anomalous Hall Effect in magnetic material and negative differential resistance phenomena in semiconductor [6]. All four basic Boolean logic operations could be programmed with high output ratio (> 1000 %) and low magnetic field ( $\sim$ 5 mT). This device demonstrated that non-volatile information reading, processing and writing could be realized in one step and one device. Hence, logic and non-volatile memory could be closely integrated in one chip. The time and energy used in the processes of information transformation and transfer could be saved. A network with these highly parallel logic-memory devices could perform massively parallel non-volatile computing and might offer a possible route to approach brain-inspired artificial intelligence beyond traditional CMOS route.



Fig1. The structure of spin-logic device.

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#### A17: Low-Dimensional Nanomaterials for Flexible Memory Devices

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With the rapid development of information technology, scientists are searching for emerging memory devices beyond Moore's law to make true leaps in sustaining data storage growth for More Moore and creating functional diversity for More than Moore. Numerous emerging memory devices based on inorganic, nanomaterials, organic and polymer materials, and their composites have been reported, such as resistive-switching memories (also named memristors), phase-change memories, ferroelectric memories, and spin memories. In this presentation, the opportunities and challenges facing memory technologies will be introduced briefly, recent advances in flexible resistive switching memories are summarized, with the merits of simple two-terminal structure, easy-way manufacturing, and multilayer stacking for high density data storage. Then, a class of novel resistive switching memory devices based on low-dimensional nanostructures have been successfully fabricated through composition modulation and interfacial engineering, with the function of nonvolatile WORM, Flash and volatile DRAM. [1-13] Furthermore, several multifunctional memory devices, including flexible and stretchable memories, multimode memories and transient memories, have been constructed. Moreover, these memory devices could be solution processed, which enable a mass-production with low-cost potential. Our study not only paves a way to design emerging flexible memory technologies based on nanostructures, but also boosts the development of nano-electronics and flexible electronics.



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#### A18: Polymeric foams for flexible and highly sensitive low-pressure capacitive sensors

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Flexible low-pressure sensors (<10 kPa) are required in areas as diverse as blood-pressure monitoring, human–computer interactions, robotics, and object detection. For applications, it is essential that these sensors combine flexibility, high sensitivity, robustness, and low production costs. Previous works involve surface micro-patterning, electronic amplification (OFET), and hydrogels. However, these solutions are limited as they involve complex processes, large bias voltages, large energy consumption, or are sensitive to evaporation. We report a major advance to solve the challenge of scalable, efficient and robust e-skin (1-2). We present an unconventional capacitive sensor based on composite foam materials filled with conductive carbon black particles. Owing to the elastic buckling of the foam pores, the sensitivity exceeds 35 kPa<sup>-1</sup> for pressure <0.2 kPa. These performances are one order of magnitude higher than the ones previously reported. These materials are low-cost, easy to prepare, and display high capacitance values, which are easy

to measure using low-cost electronics. These materials pave the road for the implementation of e-skin in commercialized applications.



Fig1. A. Schematic view of polymeric foam filled with conductive pores. B. Slice views of the internal structure of the CB/PDMS porous material (SEM, scanning electronic microscope), scale bars: top, 300 µm and bottom, 100 µm.



Fig2. A. Schematic illustration of the capacitive pressure sensor as blood pressure sensor.
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#### A19: Inspection of structure by electromagnetic and vibration type actuator

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In every country, the construction of large steel bridges, such as cable-stayed bridges, is carried out actively, and the number of bridges has been progressively increasing. Therefore, it is important to determine the detailed state of cracks and stress in a bridge. A lightweight robot and with superior operability is expected. In the present study, a novel magnetic actuator system capable of movement on a magnetic substance is proposed. Fig. 1 shows the magnetic actuator of a rotary movement type combining a magnetic wheel composed of two iron disks and an electromagnet and the electromagnetic-vibration type actuator proposed by the authors in a previous paper [1-2]. Two electromagnetic-vibration type actuators are held by an E-shaped acrylic material, and rotate two iron disks by using the reaction force of the vibration type actuator. Details of design and operation principle will be shown in a full paper. This rotary movement actuator is composed of the two vibration components, two shape-memory-alloy (SMA) coils labeled A and B, two iron disks, electromagnet and E-shaped acrylic frame. By passing an electric current through the electromagnet, a magnetic path is formed between the iron structure and the two magnetic wheels. The rotary movement actuator is 40 mm in length, 40 mm in height, 40 mm in width, and the total mass is 65 g. In this rotary movement actuator, both slide-on-ceiling and wall-climbing motions are possible. In order to improve propulsion characteristics and correspond to step movement as shown in Fig. 3, a magnetic actuator system combining two rotary movement actuators with flexible silicone rubber was prototyped. E-shaped acrylic frame was redesigned for step movement. Fig. 4 shows photograph of the actuator system. The actuator system is capable of moving 10 mm steps. In addition, over 360 degrees in all

directions, the actuator system is able to turn at a speed of 10 degrees/s. Devices other than

the above actuator systems are also scheduled to be announced. In the future, it is planned to try visual inspection of the structure with these actuators.



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#### A20: Stretchable oxide electronics for sensing applications

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Incorporating electronic materials into conformal platforms enables the development of sophisticated, stretchable electronic devices. Metal oxides, often processed at high temperatures, are attractive functional materials for a variety of electronic and optoelectronic applications. They exhibit stimulus-dependent transduction, and this change of state can also change functionality. Utilisation of oxides in stretchable devices has been limited due to technological challenges. Rendering oxides stretchable will be key to unlocking new fundamental properties such as envisioning strain as a new stimulus as well as to create novel high-performance conformal devices. The concept of using oxides as passive sensing elements also offers a potential solution to power hungry wearable devices.

We have created a patented transfer process<sup>1</sup> which uses the naturally weak adhesion of platinum to silicon to render oxides stretchable. This process results in a unique 'micro-tectonic' surface, which is applicable to multiple oxide platforms and facilitates new stretchable device applications. This process has been demonstrated using transparent indium tin oxide<sup>2</sup>, zinc oxide<sup>3</sup>, and titanium dioxide<sup>4</sup> thin films (all deposited at high temperatures) with stretchability of up to 15%, which is exceptionally high for a brittle oxide. The microtectonic phenomenon has been used to demonstrate gas and UV sensors and optical devices. Recently, the team have also fabricated stretchable devices using materials such as vanadium oxide and strontium titanate<sup>5</sup> which unlocks novel applications with multi-stimuli sensing and memory devices.

The presentation will cover the challenges faced and overcome, device performance, insights obtained and new opportunities which are presented through these stretchable oxide based electronic devices.



Fig1. (a) Stretchable and transparent zinc oxide on PDMS, (b) Nano-fabricated titanium dioxide on PDMS

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### A21: Carbon Nanotube for Wearable and Robust Electronics

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# A22: Oxide Semiconductor Based Diodes, Transistors, and Circuits for Wearable Electronics

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Novel thin-film materials, particularly the fast-developing oxide semiconductors, can be intrinsically flexible and transparent while in the meantime maintain high carrier mobility. However, the long anticipated flexible mobile phones and wearable electronics have not yet been commercialized due to two obstacles: a) lacking flexible diodes and transistors that are fast enough for wireless communications; and b) lacking flexible circuits with low power consumption.

Here, based on oxide semiconductor amorphous InGaZnO, with material optimization and device engineering, we developed flexible Schottky diodes at a record speed of 6.3 GHz in 2015,

[1] and demonstrated the GHz thin-film oxide transistors in 2018. [2]

The lack of satisfactory p-type oxides highly limits the realization of oxide CMOS electronics to enable low power transistors necessary for wearable and portable electronics. Based on our efforts on p-type SnO transistors,[3,4] we demonstrated various CMOS circuits with p-type SnO and n-type InGaZnO, including inverters, logic gates, ring oscillators, full adders, D-latchs, SRAM, etc., all with low power consumption of pW~nW, full amplitude outputs, and excellent noise margins [5,6,7]. The maximum CMOS integration scale of 104 transistors reaches a record high for the all oxide semiconductor based CMOS circuits. [7]



- Fig1. The structures and performances of a 6.3 GHz InGaZnO Schottky diode (top left), a 1.2 GHz InGaZnO thin film transistor (TFT) (bottom left), and a pw-nw powered CMOS invertor based on p-type SnO and n-type InGaZnO (top right); the layouts of several CMOS circuits based on p-type SnO and n-type InGaZnO (bottom right).
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#### A23: Rigid Plastic Models for Metallic Porous and Powder Materials

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The constitutive equations of a wide class of rigid plastic models for porous and powder materials comprise a pressure-dependent yield criterion and its associated flow rule. Therefore, the material response is completely controlled by the yield criterion. In contrast to pressure-independent plasticity, a great variety of yield criteria is available in the literature. Even though the corresponding yield surfaces may be close to each other in stress space, mathematical features of the equations and solutions are rather sensitive to the yield criterion. The present article concerns plane strain problems. The corresponding equations may belong to hyperbolic, or elliptic or parabolic type. In the case of hyperbolic systems, the equations for characteristic curves and characteristic relations are derived and discussed. The characteristic coordinates can be used for solving boundary value problems. It is shown that the method of moving coordinates, which is well known in plasticity of pressure-independent materials, can be generalized on some models of pressure-dependent plasticity. Another special system of coordinates is associated with principal stress trajectories. It is shown that the scale factors of this coordinate system satisfies a simple algebraic equation, which can be used for solving boundary value problems [1].

Another class of rigid plastic models for powder materials is based on the double-shearing concept. The present article is restricted to the double-shearing model

(Spencer's model). In addition to the mathematical features of solutions above, solutions for the double-shearing model can be singular. In particular, some components of the strain rate tensor approaches infinity according to an inverse square rule in the vicinity of envelopes of characteristics [2].

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### A24: Evolution of Iron(II) Spin Crossover Hofmann-like Metal-Organic Framework Materials

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The multi-functional properties of spin crossover (SCO) coordination compounds in association with smart materials are promising materials for components of memory devices, displays, sensors, mechanical devices, and especially actuators such as artificial muscles. Studies aimed at producing attractive SCO complexes are advancing, and they are associated with different aspects of material chemistry that majorly use <sup>57</sup>Fe Mössbauer spectroscopy with a complementary measurement technique like SQUID[1]. 3-d orbital block-transition metal coordination compounds with d<sup>4</sup>–d<sup>7</sup> configuration in an octahedral crystal field exhibit a potential for SCO between the low spin (LS) and the high spin (HS) states. Octahedral iron(II) SCO systems with 3d<sup>6</sup> represent candidates for species switchable between the diamagnetic ( $t_{2g}$ )<sup>6</sup> and the paramagnetic ( $t_{2g}$ )<sup>4</sup>( $e_g$ )<sup>2</sup> configurations. Iron(II) coordination polymers with bistable systems between the LS and the HS states that are usually triggered by external stimuli, including temperature, light, nuclear decay, pressure, and the inclusion of guest molecules, are a class of potential substances for smart materials.

In the group of Hofmann-like coordination polymer SCO materials, the one-step SCO in Fe<sup>II</sup>(pyridine)<sub>2</sub>Ni(CN)<sub>4</sub> was by chance discovered using <sup>57</sup>Fe Mössbauer spectroscopy and SQUID measurements in 1996 during studies of the Hofmann-type clathrates Fe<sup>II</sup>(NH<sub>3</sub>)<sub>2</sub>Ni(CN)<sub>4</sub>.2G, which do not act as SCO[2]. SCO Hofmann-like metal-organic

frameworks containing two dimensional (2D) layers and 3D structures with octahedral iron(II) ions linked by cyanidemetallates along the in-plane directions were investigated thoroughly to develop new SCO materials for applications in smart materials [3]. The hot atom chemistry is linked to over ranges in the effects of chemical properties. Among the hot atom chemistry linked to radio-analytical nuclear sciences, the nuclear-decay-induced excited spin state trapping for the <sup>57</sup>Co-labeled Hofmann analogous compound <sup>57</sup>Co(pyridine)<sub>2</sub>Ni(CN)<sub>4</sub> is very important for switching behaviors. These are demonstrated using the emission Mössbauer spectroscopy in powerful and sensitive nuclear probes for obtaining local daughter site information [4]. We found that a soft X-ray-induced excited spin state trapping effect occurs in Hofmann-like SCO coordination polymers of Fe<sup>II</sup>(4-methylpyrimidine)<sub>2</sub>[Au(CN)<sub>2</sub>]<sub>2</sub> and Fe<sup>II</sup>(pyridine)<sub>2</sub>[Ni(CN)<sub>4</sub>]. Measurements using soft X-ray absorption spectroscopy on these polymers indicate that the HS (S = 2) is prevalent in iron(II) ions even at temperatures significantly below the critical transition temperatures, inducing HS states trapping due to the X-ray irradiation.[5].

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#### A25: Li Diffusion in Garnet-type Electrolytes studied by the PFG NMR Spectroscopy

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Ion-conducting garnets are important candidates for use in all-solid Li batteries. The Li<sup>+</sup> diffusion behavior is essential for understanding ion conduction mechanisms. Actually, Li-diffusion phenomena have been widely studied for solution electrolytes used in LIB, ionic liquids, and solid electrolytes.<sup>1</sup> Proposed nano-scale lithium pathways are composed of tortuous and narrow Li<sup>+</sup> channels. The pulsed-field gradient (PFG) NMR method provides the time-dependent Li<sup>+</sup> diffusion information in the micrometer space, where the Li movement must be different from the simple extension of the nano-space behaviors. The Li<sup>+</sup> diffusion observed by the PFG-NMR is very anomalous, and depends on the measuring parameters; observation time ( $\Delta$ ) and the pulse field gradient (PFG) strength (g). The Li<sup>+</sup> diffraction patterns are observed in short  $\Delta$ , which were induced by the Li collision in the Li diffusing channels.

Centimeter-size single-crystal garnet samples were grown by the floating zone method. The anomalous Li diffusion behaviors in the powder samples were reduced in the single crystal samples. We prepared three single-crystal cylindrical-shape samples of LLZO-Ta as SC-A, B, and C of which sizes were 4-mm diameter and 6-mm height. Also a crushed sample from the single crystal sample was prepared. The collision-diffraction patterns in the echo attenuation plots for the three single-crystal samples with  $\Delta = 10$  ms (Fig. 1 (a)), and those for the crushed sample with  $\Delta = 10$ , 20, 30, and 40 ms are shown in Fig.1 (b). The inner morphologies are clearly reflected in the NMR echo-attenuation plots. The experimental findings in the Li<sup>+</sup> diffraction in the garnet powder samples<sup>2.3</sup> are well interpreted by using single-crystal garnet samples (Li<sub>6.5</sub>La<sub>3</sub>Zr<sub>1.5</sub>Ta<sub>0.5</sub>O<sub>12</sub> (LLZO-Ta) and Li<sub>6.5</sub>La<sub>3</sub>Zr<sub>1.5</sub>Nb<sub>0.5</sub>O<sub>12</sub> (LLZO-Nb)).<sup>4</sup>



Fig1.(a) q-Space plots of echo attenuation for collision-diffraction patterns of (a) the SC-A, SC-B and SC-C samples with  $\Delta = 10$  ms (inner quality was the best (SC-A), better(SC-B) and SC-C included cracks) and (b) the crushed samples with  $\Delta = 10$ , 20, 30 and 40 ms at 35 °C, g = 10.0 Tm<sup>-1</sup>, and  $\delta$  was varied up to 8 ms (60 points). For longer  $\Delta$ , the diffraction patterns became smoother and completely disappeared for  $\Delta = 40$  ms.

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### A26: Towards understanding gas flow in functionalized mesoporous membranes

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In microfluidic systems, energy and separation science, surface functionalizations of inorganic substrates are an active field of research. Especially for gas separation, mesoporous materials are often functionalized, for example in gas chromatography columns or in gas separation membranes. While chromatography columns usually have homogeneous stationary phase, inorganic membranes are prepared using layer by layer deposition resulting in an asymmetric structure with pore sizes decreasing with each layer. The benefit of these asymmetric structures clearly is a low pressure drop, being able to keep the amount of layers with small sizes to a minimum while guaraneeing sufficient mechanical strength by a macroporous support. However, the downside is an increased complexity: Properties like flow or selectivity are affected by multiple gas transport mechanisms on different length scales.

In order to fully understand the transport processes and how surface functionalizations affect these on different length scales, we investigate the gas transport mechanisms in each layer independently. We achieve this by preparing homogeneous membranes possessing

monomodal pore size distributions with  $d_{50}$  between 20 and 60 nm, trypical values for intermediate layers in gas separation membranes. Similar to our previous work [1-3], the surface of these membranes are then chemically functionalized using silanes with different functional molecules showing alkyl-, phenyl-, amino- and sulfonate groups and possessing different spacer length. The gas transport is analyzed by single gas permeation measurements. Results of a large parametric study are presented using He, Ne, Ar, N<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, CO and CO<sub>2</sub> as model gases while varying the measurement temperature from 273 to 353K.

One major finding of our study is the strong dependency between the length of the functional molecule and a significant drop in gas flow. Not being able to explain this drop with the reduced pore size and porosity of the membranes due to the surface functionalization leads to the conclusion, that the transport processes have not been completely understood and that further research is needed to reveal the mechanims involved.

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# A27: Modelling the drying shrinkage of porous materials incorporating capillary and adsorption effects

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When a porous material is subjected to drying, corresponding drying shrinkage strains will occur. On the other hand restraining drying shrinkage leads to the development of stresses that could eventually cause material cracking. Therefore, a proper poromechanical model is needed in order to predict those stresses/strains and hence prevent the appearance of cracks. Different poromechanical models [1] [2] [3] based on the concepts of capillary pressure or disjoining pressure are found in the literature. However, it has been shown [4]

that those models fail to describe the evolution of drying shrinkage strains for a relative humidity lower than 40% - 50%. This deficiency can be reasonably linked to the fact that those models neglect the presence of adsorbed water on the surface of desaturated pores.

In this work, a poromechanical model describing the drying of unsaturated porous media for a large range of relative humidity is proposed. Based on a thermodynamical approach, the derived model allows to account for various contributions which include: the capillary pressure, the water adsorption, and the Shuttleworth effect [5] which recognizes that at an elastic solid interface, the surface energy is different from the surface stress. Most of the input parameters of the model, related to the evolution of the unsaturated pores volume and surface, are found by applying the B.E.T [6] and the BJH techniques [7] to the desorption isotherm of the material. The remaining input parameters, more related to the hygro-mechanical coupling (such as the Biot coefficient and a parameter that governs the magnitude of the Shuttleworth effect) can be fitted on experimental drying shrinkage strains.

The model was validated by comparing the predictions to experimental drying shrinkage strains data found in the literature. Different porous materials were studied: hardened ordinary cement paste, high performance concrete and Vycor glass. The obtained results show a satisfactory prediction of strains for the tested materials. In particular, compared to other poromechanical models found in the literature such as [1] and [8], our model appears to be exclusively able of displaying the transition at a certain relative humidity between the contribution of the capillary pressure and that of the adsorption. This transition induces a kink in the drying shrinkage strains at this value of relative humidity (See Fig1 for an example).

In the future works, the new poromechanical model will be validated by comparison with drying shrinkage tests executed in the internal laboratories of *EDF* on a high performance concrete.



Fig1. Comparison of the proposed model with the models of [1] and [8] for the experimental data of [9]

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#### A28: Design of Porous Organic Salts (POS) with Versatile Function

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Porous materials using organic molecules have attracted much attention due to their potential application for not only gas absorption but also chemosensor, bioimaging tool and so on. However, it is still difficult to construct porous structures from only simple organic molecules. Thus, we have proposed a novel hierarchical method to construct porous structures. In this method, the first step is to build up molecular assemblies. The assemblies act as a stabilizer of porous structures with larger inclusion spaces. Then, the assemblies are accumulated by various intermolecular interactions between assemblies to achieve both robustness and functionality of the porous structures. We have previously reported that organic salts composed of triphenylmethylamine (TPMA) and various sulfonic acid derivatives constructed unique molecular assemblies "supramolecular clusters" through cubic hydrogen-bonding networks. Here we demonstrate that TPMA and sulfonic acids having polyaromatic moieties give a new class of porous structures consisting of diamond networks, termed as diamondoid porous organic salts (*d*-POSs). For instance, the supramolecular clusters are hierarchically accumulated by  $\pi$ - $\pi$  interactions between the polyaromatic moieties to yield the *d*-POSs through formation of the diamond networks. Large steric hindrance of the clusters prevents the diamond networks from constructing highly interpenetrated structures, giving continuous open channels. It should be noted that the interpenetration degree of the diamond networks is controlled by tuning the bulkiness of the cluster with alteration of sulfonic acids.



Fig1. Hierarchical construction of diamonded porous organic salt.

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#### A29: Discontinuous porosity approach to study a sand-clay media mixed with foam

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During tunneling with an Earth Pressure Balance (EPB) shield, surfactants are commonly used as conditioning agents to reduce clay stickiness. The excavated soil is a sandy-clay soil conditioned with foaming agent. A possible use of this soil is limited by the consequences of this treatment on the soil properties. Few works investigate the become of soil-foam system after excavation [1-3]. This work goal is to study the foam-soil mixture properties and their behavior under the foam degradation.

This study is carried out on four reconstituted sandy clay soil composed respectively by 100% sand, 80% sand + 20% kaolin, 70% sand + 30% kaolin and 60% sand + 40% kaolin . Soils are conditioned with a foaming agent CLB F5/AC. In a soil-foam system, the soil particles prevent the evolution of the foam due to the low porosity, which increases their stability compared to foam alone [3]. The presence of the foam in the soil modifies their structure, it adds to the solid matrix bubbles of gas separated by thin films (figure 1.a.&b.). These gas bubbles are different from the conventional air present in unsaturated soils; it is not connected and the air pressure in the foam bubbles is higher than the water pressure. The approach of the discontinuous porosity generated by inclusions of gas bubbles was used to describe the media. Foam degradation is studied by following the phenomenon of drainage coalescence and coarsening which occur over time by foam volume determination.

Variation of FIR (Foam Injection Ratio) shows that there are limit FIR values from which the foam begins to be present in the soil sample with the discontinuous porosity "f" increases and continuous porosity decreases. It was demonstrate that the mixture permeability can be determined using the discontinuous porosity approach. The global evolution of foam volume percentage in the conditioned soil was analyzed by measuring the evolution of f over time. A rapid decrease over time of foam percentage in sand soil compared to clay soil was observed (figure 1.c).



Figure 1. Optical microscope photo of mixture: a. sand + foam, b. Sand + kaolin + foam; and c. Effect of foam degradation on conditioned soil porosity (total and discontinuous porosity) over time

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### A30: About Industrial Porous Materials: Limits of Pollutants Filtration within Carborundum Foam Ceramic Structures

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The present work is about Carborundum Foam Ceramic (SiC) and its filtration capacity in industrial approaches. Initially observed in 1824 by Jöns J. Berzelius in a synthetic diamond experience, by a parasite reaction between Carbon and Silice, this porous material is found much utilised since the industry of 1890, raison to its precious properties, such its great thermal conductivity, powerful resistivity to thermal shocks and chemical oxidation, not to mention its low thermal expansion.

As a function of the synthetic-temperature and the time-reaction, Carborundum Foam Ceramic could be produced with various specific surfaces, as between 10 and 20 m<sup>2</sup>/g. Similarly, the conposititon and the granulometry of the used mixture powder could control its porosity with its mean pores' diameter. For industrial applications (*as filters and catalysts*), the porosity is ranged between 37% and 45%, with mean pore diameters of about 9 to 15  $\mu$ m. Regarding the permeability "*the key factor for most industrial applications*", a large range of the latter could be denoted [1].

Industrially speaking, *Porous Materials* were adopted many years ago against the pollutant filtration problem that observed frequently in various fields, such the refining field and the pharmaceutical one. Subsequently, intensive investigations were developed to reach the perfect pollutant filtration process.

Reason to the pollutant nature, it was established that the basic filtration at low thermal buoyancies consists, usually, of steady state regime, easily controlled at pilot processes. Through increasing values of the boundary conditions (*as the temperature and the nanopaprticles' size*), the pollutant filtration process could become unstable, leading to a huge loss in both the energy cost and the used porous material. Against Viscoplastic pollutants, *as the Crude-Oil subtracts and discharge of polymer melts*, filtration process could reach another level of complexity. Over the years, several experiments have been realized and directed towards determining the extent and the mean shape of the yielded/unyielded regions into the porous structure, in order to avoid the quick clogging into its inter-pores, as these regions are the pre-eminent feature of viscoplastic pollutants.

One of the ways to pilot the lost energy into such a system is to adopt the SiC Porous Material. By taking annulus shapes as an example, the generation of a high pressure gradient between the annulus limits could increase the filtration efficiency. But critical situations will be reached, as the new complex structures and the inner sub-flow regimes over the process time.

Face to such big challenges, our alternative will be mathematical modeling. In view of the fact that the nature of industrial processes is often non-linear, extremely complex and not sufficiently recognized, the development of the primary conditions for better filtration optimization is of practical significance. As such, our presentation in Porous Materials Conference will be undertaken to extend the pollutant buoyancy-range and the critical aspect ratio of various shapes of SiC filters to make accurate information about filtration stability, using Carborundum Foam, and the evolution of the porous structure during the operation time.



Fig.1 Nanoparticles' deposition onto the Carborundum Foam Ceramic after filtration.

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# A31: Porosity characterization of wet solids: DSC thermoporometry and 1H NMR relaxometry

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Surface characterization of materials (e.g. adsorbents) in wet state is not possible by well-established methods of gas sorption (drying is necessary before testing). Contrary, it is obvious that porosity of materials differs in dry and wet state and this is the reason why results of adsorption experiments in aqueous media are often in poor relation to gas sorption based characteristics. Therefore, methods of porosity characterization in wet state should be sought. Our contribution focuses on two alternative methods suitable for this purpose: thermoporometry by DSC and <sup>1</sup>H NMR relaxometry.

Thermoporometry is based on depression of melting/freezing temperature of a liquid entrapped in the pores, which is caused by the small size of crystals formed inside the pores. If water is used as probe liquid, the measurement can be simply performed on any common DSC apparatus after appropriate optimization (details for porous carbons can be found in [1]). With the use of appropriate parameters (which can depend on studied material) the experimental DSC record can be directly transformed to pore size distribution. The lower limit of measurable pore sizes arises from the temperature limit where solid – liquid transition disappears ( $\approx 2$  nm).

Porosity characterization by <sup>1</sup>H NMR relaxometry is based on the fact that speed of relaxation of magnetized nuclei depends on the mobility of molecules. This parameter depends for liquids (e.g. water confined in pores) on the size of domains occupied by the liquid. Thus hydrogen nuclei of water molecules entrapped in small pores relax much faster than in bulk water. The analysis of experimental relaxation curve rests in finding of number of components connected with differently relaxing protons present in studied system. The appropriate parameters, amplitude and relaxation time, corresponding with given types of protons can be non-linear optimized and used for characterization of pore size distribution of various porous materials.

For illustration of applicability of both techniques the Figure 1 shows comparison of pore size distribution obtained by thermoporometry and <sup>1</sup>H NMR relaxometry for mesoporous carbon with result of standard sorption of nitrogen at 77 K. Appropriate volumes of mesopores (for NMR calculated from the peak around 10 - 25 nm) determined from alternative techniques (thermoporometry - 0.916 cm<sup>3</sup>/g, <sup>1</sup>H NMR relaxometry – 0.918 cm<sup>3</sup>/g) agree well with the value obtained from nitrogen sorption (0.958 cm<sup>3</sup>/g).



Fig 1. Comparison of pore size distribution obtained by nitrogen sorption, thermoporometry a <sup>1</sup>H NMR relaxometry.

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### A32: A self-standing supercapacitor electrode based on MOF-derived NiO/C@CNF composite

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NiO has been widely studied as a pseudocapacitor material because of its low cost and high theoretical specific capacitance (2584 F g<sup>-1</sup>). [1] Despite its high specific capacitance, in practice, NiO still suffers from restricted specific capacitance that is lower than its theoretical value and poor rate performance during charge-discharge process due to the inherent low electrical conductivity of NiO. To solve the problem, significant efforts have been devoted including: (1) Nano-structured NiO. [2-3] Nano-structures could increase the contact areas between electrolyte and electrode, and facilitate ion insertion/desertion.; (2) Composite with carbon materials. [4-5] Metal oxide-carbon composites could improve electrical conductivity of metal oxides and provide additional electric double-layer capacitance. Recently, NiO synthesis methods that satisfy all of the above 2 approaches have been reported using Metal-organic frameworks (MOFs). [6-7]

In this work, we present a new combination of nickel oxide-carbon composites by directly carbonizing Ni-MOF@CNF for supercapacitor as shown in figure 1. The nano-sized NiO derived from MOF is uniformly distributed in the carbon matrix, improving the performance of NiO. The 3D interconneted structure, the MOF is grown on the surface of CNF, enables fast electron transfer and also serves as a self-standing electrode without current collector. This self-standing electrode shows a high specific capacitance of 672.72 F g<sup>-1</sup> at 1 A g<sup>-1</sup> and 581.82 F g<sup>-1</sup> at 10 A g<sup>-1</sup> in 3 M KOH, indicating an excellent rate capability. An Asymmetric supercapacitor is constructed from NiO/C@CNF with activated carbon (AC) with a potential from 0 to 1.6 V. It shows also an excellent specific power of 1,454.55 W kg<sup>-1</sup> at a current density of 1 A g<sup>-1</sup>. Furthermore, the asymmetric supercapacitor shows good stability towards long time charge-discharge cycle test.



Fig 1. Illustration of the synthetic process and reaction mechanism of NiO/C@CNF

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#### A33: New Flexible Hybrid Electronics Technologies for Biomedical Application

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A technological platform is established for scalable and high-performance flexible hybrid electronics (FHE) based on an advanced wafer-level packaging (WLP) methodology<sup>1)</sup>. Thin and small dielets are embedded in flexible substrates such as flexible epoxy, polydimethylsiloxane (PDMS), and hydrogel. These dielets can be interconnected through high-density wirings formed in wafer-level processing. We demonstrate heterogeneous integration of Si and III-V dielets with various thicknesses ranging from 50 to 200  $\mu$ m. High-density die-to-die interconnections are implemented over a stress buffer layer (SBL). The SBL is a key element are inserted between interdielet wirings and the substrate to mitigate mechanical stress and enhance wire reliability. 10- $\mu$ m-width Au wires are successfully formed on the SBL/flexible substrates and exhibit high bendability with a bending cycle of beyond 1,000 (bending radius: 10 mm or less). We propose and fabricate new FHEs: the applications are listed in Fig. 1 where (a) trans-nail photoplethysmographic (PPG) sensors with LED driver and photodiodes for biomedical/healthcare application, (b)

retina prosthesis 3D-IC with TSV, (c) flexible neural probes embedding micro LEDs for optogenetics, and (d) Hydrogel-based FHE for smart contact lens etc. Characterization of their mechanical and electrical properties are also introduced. These highly integrated FHEs would be expected for future wearable and implantable flexible devices toward upcoming Internet Of Everything (IoE) society with AI (Artificial Intelligent).



Fig1. Applications of new Flexible Hybrid Electronics (FHE) with embedded dielets

T. Fukushima, A. Alam, A. Hanna, S. C. Jangam, A. A. Bajwa, and S. S. Iyer, *IEEE Trans. on Components, Packaging and Manufacturing Technology*, vol. 8, pp. 1738-1746, 2018.

### A34: Polymer Assisted Deposition of Epitaxial Oxides Thin-Films and Multilayers

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Chemical solution methods are a versatile and inexpensive tool in Nanoscience particularly employed for the synthesis of complex oxides nanostructures (nanoparticles, thin films, fibers, etc.) but with some limitations for smart applications and fundamental studies. In this light, Polymer Assisted Deposition (PAD) [1] is a water-based path for the synthesis of epitaxial oxide ultrathin-films of variable structures (perovskites, spinels, garnets, etc.) and capable to stabilize metastable and elusive phases. [2] The stability provided by the polymer in the metal solution and the control over the deposition parameters achieved in PAD are suitable for the fabrication of high quality single-crystal nanostructures [3], homogenous large area coatings (Fig. 1) [4], and to add enhanced functionalities in technological substrates such as silicon in combination with physical deposition techniques. [5]

In this presentation I will describe the PAD protocol and review the last results obtained with this method as well pending challenges to apply this chemical route in flexible substrates.



Fig. 1. 1"-STO substrate with an 18 nm thick LSMO thin-film deposited by PAD.

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#### A35: Hybridizing SMD technology with inkjet Printed Circuit Board

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Inkjet-printed devices such as memristors are still unstable in air and have poor performances compared with well established silicon technology [1]. In fact, the development of advanced inks of new materials is still a challenge [2]. However, the current electronics applications require a high degree of reliability and quality of their properties. To accomplish these application requirements, hybrid electronics is fulfilled by combining the advantages of the printing technologies with the surface-mount technology. In this work, silver nanoparticles-based ink is used as method to connect surface-mount devices (SMDs) onto inkjet-printed pads, conducted by inkjet printing technology. Excellent quality device-pad junctions are ensured with high resolution picoliter drop jetting at low temperature (~150 °C). Electrical, mechanical and morphological characterization is carried out to assess the performance of the junction. As shown in fig 1 (left), inkjet bonded devices are compared with common benchmark materials for SMT bonding (i.e. silver epoxy and solder). Electrical contact resistance characterization shows similar performance between SNPI and the usual ones. Mechanical shear strength characterization shows comparable ultimate load for SNPI and silver epoxy, and both present higher adhesion than solder. Morphological inspections by field-emission scanning electron microscopy confirm a high quality interface of the silver nanoparticles interconnection. Finally, a flexible hybrid circuit on paper controlled by Arduino board is manufactured, demonstrating the viability and scalability of the SNPI assembling technique (fig 1, right).



Fig1. Left, SMDs bonded by inkjet method and silver epoxy on paper, Kapton and glass. Right, hybridized Inkjet-SMD circuit on paper [3]

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# A36: Novel Antennas and RF Structures for Wearable Technology and IoT Applications

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### Abstract:

Recent years have witnessed extensive research activities in the field of wearable and flexible electronics. As of 2015, it has been estimated that there are around 1500 worldwide research groups/centers working on diverse aspects of flexible and wearable electronics.

Consistently, wearable electronics would often require the integration of antennas operating at specific frequency bands to provide wireless connectivity which is highly

demanded by today's information oriented society. Wearable wireless systems are applied in a wide spectrum of fields which include but are not limited to: personal communication, medicine, military, industry, entertainment, and aerospace.

In this talk, the development, fabrication process, and characterization of wearable antennas and RF structures are presented. Furthermore, novel wireless system designs dedicated for practical applications are discussed in detail.



A Flexible Antenna for Integration within Wearable Wireless Systems. (Photo by Haider Raad ©)

# A37: Ultra-thin Langmuir–Blodgett thin films: Gas sensing and energy harvesting applications

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Current research in energy harvesting and gas sensing require architecture optimization, process improvement, interface engineering and scale-up. Ultra-thin and uniform semiconductor films have been investigated widely in fields of optoelectronic, photonic, gas sensing and energy storage/harvesting in order to improve the device performances. Conventional methods of preparing ultra-thin films, such as thermal evaporation, electron-beam evaporation, or hot-filament vapor deposition may not be very useful in terms of large area device fabrication for commercial scale-up. Langmuir–Blodgett (LB) technique, on the other hand, is very useful technique for preparing regular multilayers with controlled thickness on a large area and obtaining a well-defined molecular orientation.

At our organization, we have been preparing Langmuit-Blodgett of metal oxides as well as conducting polymers for various applications [1-3]. In general, the metal oxide based LB films were prepared by thermal or UVO-decomposition of the corresponding LB multilayers of precursor containing metal salts. The conducting polymers LB films of polycarbazole and MEH-PPV were prepared using appropriate solution. The deposition parameters were optimized and films were used for various gas sensors such as H<sub>2</sub>, H<sub>2</sub>S and NH<sub>3</sub> as well as energy harvesting application such as solar cells and hydrogen generation. In this talk, I will present work carried out at BARC to demonstrate the application of LB thin films in the application swill be discussed. In conclusion, the challenges faced to prepare LB films will be addressed.



Fig. 1. (a) XRD pattern of as-deposited LB film of ODA-palladate and PdO thin film. (b) SEM image and (c) H<sub>2</sub> gas response of PdO film

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### Poster

# P01: Optimization of oxygen chemisorption on the carbon surface based on kinetic analysis of isothermal thermogravimetry

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The kinetics of carbon oxidation at low temperature (<300 °C) was explored by isothermal thermogravimetry in order to predict the optimal conditions (temperature, oxygen content) to obtain the maximal amount of oxygen on carbon surface (in more detail described in [1]).

Thermal oxidation experiments (TG-DSC) were performed using SetsysEvolution (Setaram) instrument. At first, the nonisothermal thermogravimetric experiments were performed by heating a sample of carbonaceous material in an oxidizing atmosphere (20, 50 and 80%  $O_2:N_2$ ) at a rate of 10 K min<sup>-1</sup> to a temperature of 1000 °C. Based on nonisothermal experiments, the temperatures appropriate for the isothermal study of surface oxidation of carbonaceous materials were determined (200, 220, 240, 260 and 280 °C). In the case of isothermal experiments, the samples were at first heated up to the working temperature under an inert atmosphere (nitrogen) and the oxidizing atmosphere was introduced into the system after the selected temperature was maintained. The isothermal oxidation measurements were recorded for 2 h.

Based on performed TG-DSC isothermal experiments, it can be assumed that the course of low temperature oxidation of carbonaceous materials can be described by three reactions: i) formation of oxygen-containing functional groups, ii) oxidation of carbonaceous materials itself leading to the combustion of the sample, and iii) decomposition of created oxygen functional groups.

This model of three reactions was used to obtain the kinetic equation of the whole process, which allows to simulate oxidation under the different conditions and to find out the optimal parameters for the maximum extend of surface oxidation. A truncated Sestak-Berggren kinetic model was used to describe the oxidation of carbonaceous materials and the common apparent kinetic parameters were found by non-linear regression.

The optimized kinetic equation has shown the good agreement between the theoretical and experimental data and enabled calculation of conditions for effective carbon surface oxidation (maximal oxygen chemisorption). Predicted oxygen uptake at given conditions (4.0% at 226 °C in 20%  $O_2$ , 4.6% at 196 °C in 50%  $O_2$  and 4.5% at 205 °C in 80%  $O_2$ ) was confirmed experimentally with very good agreement (e.g. Figure 1 (a) for 50%  $O_2$  atmosphere).

When the dependence of oxygen pressure was incorporated into the kinetic equation, the model becomes less reliable and its prediction strength decrease. The discrepancies (Figure 1 (b)) were probably caused by the impropriate description of the pressure dependence (model  $p_{02}^p$ ). Development of better models for description of the effect of gaseous reactants in heterogeneous thermal reactions serves a challenge for future work.



Fig1. Comparison of the theoretical TG curves (*teor*, black line) of the maximal oxygen chemisorption on the carbonaceous sample surface with the experimentally (*exp*, grey points) measured data in the atmosphere of 50% (a) and 100% (b) of oxygen.

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# **P02:** Characterization of porous carbon paper electrode prepared from the bleached rice husk pulps for supercapacitor application

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With the limits of the increase in the use of fossil fuels, energy lacks have become energy difficulty and thus have been required to develop a new eco-friendly and a high efficiency energy storage device. The supercapacitor categorized as electric double-layer capacitors (EDLCs) have been growing due to their high-power density, fast charge/discharge rates, low environmental pollution, and great cycling performance [1, 2]. The performance of EDLCs is mainly affected the structure of the electrodes, the sort of electrolyte, and the interaction of the electrodes and the electrolyte. The primary mechanism of EDLCs depends on the pore walls of their materials. High porosity related with a high surface area is required to increase amounts of a charge storage. Activated carbon materials play important roles as electrode materials and have been used to manufacture EDLCs such as generally available commercial device. This reason is due to excellent electrochemical performance by their high surface area, tunable pore size, chemical resistance, non-corrosion, and good electrical conductivity. However, the precursors of most of carbon materials are usually derived from fossil fuel. These will badly affect various environmental conditions. The growth of green and renewable energy source materials is required. Rice husks which are also called "Rice hulls" are the outer shells covering the rice kernel. These materials are one of agricultural byproducts produced from rice processing. Its chemical compositions are similar to those of many usual ligno-cellulose fibers which consist of cellulose, lignin, ash, and moisture. However, rice husk, from now, has been used as a fuel, feedstuff and fertilizer in some countries, or else it was burnt or dumped as wastes. Sometimes, these burnt and dumped rice husks can become the cause of the environmental pollution. However, rice husks are one of the most widely potential and available agricultural materials. We prepared cellulose papers using rice husks which were alkali-cooked and bleached through 2 step bleaching process. The obtained cellulose papers are carbonized at 900 °C during 1 h under an atmosphere of highly pure nitrogen (99.999%). To prepare activated carbon papers, the obtained carbon papers was mixed with 20 wt% KOH solution and dried at 80 °C. The carbonization was performed at 500 °C, 700 °C, 900 °C and 1100 °C, respectively for 1 h under nitrogen atmosphere. The obtained activated carbon paper was subsequently washed with 0.1 M H<sub>2</sub>SO<sub>4</sub> and distilled water until neutral and then dried at 80 °C. Activated carbon papers are characterized by SEM, FT-IR, XRD, and BET. Electrochemical performance of activated carbon papers as electrode were investigated by cyclic voltammetry (CV) and galvanostatic charge tests using a CHI 660E electrochemical workstation.



- Fig1. (a) Activated carbon paper obtained from the bleached rice husk pulps. (b) CV curves (scan rate of 50 mV/s) and (c) GCD curves (current density of 0.1 A/g) of activated carbon papers obtained from various high temperature.
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#### P03: The effect of ILs as co-salts in electrolytes for high voltage supercapacitors.

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Ionic liquids (ILs) which have electrical stability are attractive materials to enhance the potential window of electrolyte. According to the potential window is extended, available voltage for supercapacitor is broaden. In this study, the addition of ILs which is 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF4) and 1-ethyl-3-methylimidazolium bis(trifluoromethylesulfonyl) imide (EMITFSI) as co-salts, to a supercapacitor electrolyte increases the ionic conductivity and stability of it due to inhibition of electrolyte decomposition. As a result, the electrochemical stability potential windows (ESPWs) of supercapacitor is improved and the supercapacitor exhibited increased cycling stability. The loss of specific capacitance upon addition of 7 wt% EMIBF4 or EMITFSI to the electrolyte was 2.5% and 8.7%, respectively, after 10,000 cycles at 3.5 V, compared to the specific capacitance of the initial discharge.

#### P04: The effect of porosity on sorption properties of oxide materials

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Hydrogen is a very attractive source of energy, however its use is marred with many problems like high cost of storage, transport and distribution. One approach to solve these problems or circumvent them is the search for new materials allowing its effective storage. At present the solid state storage seems to be the most promising [1]. The materials used for hydrogen storage include: metal hydrides, organometallic compounds or carbon-based materials [2-4]. In these systems the hydrogen molecules are stored in mesoporous materials by employing the physisorption (characteristic of weak van der Waals interactions). In physisorption, the adsorption capacity of a given material is proportional to its surface area [5-7]. Storage based on adsorption permits reduction of the total pressure in the system so increases the safety of work. Moreover, the volume and cryogenic limitations can be overcome. In the last few decades many materials for hydrogen storage have been designed and characterized, including alloys, nitrates, oxides etc. [8].

The aim of our study was to check the possibilities of using oxides, obtained by the sol-gel method, for hydrogen storage. The proposed materials are based on aluminum oxide and boron oxide produced in the form of films. The sol-gel method permits control of formation of the adsorption system, which means that the textural properties of the system can be tailored.



Fig1. Al<sub>2</sub>O<sub>3</sub> film

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#### P05: Porous organosilanes as potential sorbents of hydrogen

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The search for new methods for hydrogen storage has recently attracted much attention because of the necessity of using ecological sources of energy to limit the emission of environmentally harmful substances produced when using fossil fuels. Storage of hydrogen in a solid state based on the process of adsorption or chemisorption on a highly developed surface would permit replacement of containers for liquid hydrogen or pressured gas hydrogen with a solid state material containing large amounts of hydrogen [1]. At present the most popular hydrogen storage materials are carbons of high surface area and nanomaterials based on carbon [2,3]. The ability to absorb hydrogen depends on the surface area and pore size, which stimulates interest in nanomaterials and their use in new technologies and technological innovations. The hydrothermal method permits obtaining nano-scale materials in a closed system under the pressure of solvent that can be water or anhydrous solvent [4]. Development of the hydrothermal method for obtaining powder materials is expected to lead to new materials that will show potential for hydrogen storage.

A very interesting class of new hybrid inorganic-organic compounds, known as mesoporous organosilicons (PMOs) has opened a new area of applications of porous materials [5-6]. PMOs are obtained by hydrolysis and condensation of (RO)3Si–R0–Si(OR)3 in the presence of a template. PMOs materials show unique chemical, physical and mechanical properties which make them attractive in a wide range of applications, e.g. in catalysis, adsorption, separation. It is known that pure silicas or organosilicas are inactive in many reactions, however, incorporation of metals such as Al, Ti permits generation of new active centers. We have designed a method for obtaining porous silicon-aluminum materials of different Si/Al that seem attractive for hydrogen storage.

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# P06: A study on a hybrid index matching layer of the Mn-SnO2/Ag/Mn-SnO2 tr i-layer film on PET substrate

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It was known the presence of an index matching layer can reduce the amount of reflection between the adbesive – transparent conducting electrode interface, which in turn, can reduce the interference of reflected light and the appearance of fringes on the touch sensor panel. So far not many works have been undertaken to study the modification of optical properties through the addition of index matching layers into OMO, tri-layer structures. Initially, a hybrid structure of Mn doped SnO2 (MSO)/Ag/ Mn doped SnO2 (MSO) was deposited on PET substrate by sequential RF/DC magnetron sputtering at room temperatur, whereas spin-coating was used to deposit PDMS at various dilution ratios in

<sup>2019.</sup> 

hexane. Optical and electrical properties were systematically investigated as a function of MSO thickness and oxygen partial pressure. In order to estimate the optical characteristics and compare them with experimental results in advance, the simulation program named EMP (Essential Macleod Program) was adopted. Pattern visibility was examined by comparing the differences in the color and reflectance of oxide/metal/oxide multilayers before and after adding the PDMS and MTO IMLs. Fig.1. shows a schematic diagram of the MTO/Ag/MTO/PDMS/MTO multilayer film in the unetched region (R2) and the PDMS/MTO/PET film in the etched region (R1). In addition, the effects of the PDMS dilution ratio on the electrical and optical characteristics were also investigated. The MTO/Ag/MTO/PDMS/MTO multilayer films showed high transmittance (>86% at 550 nm) except at the dilution ratio of 1:50. As the PDMS dilution ratio increased from 1:50 to 1:200, the reflectance difference ( $\Delta$ R) increased from 0.08% to 0.35% and the color difference ( $\Delta$ b\*) increased from 0.31 to 1.23. The maximum resistance changes of the multilayer films were 0.126% and 0.124% after outer and inner bending, respectively, for 10,000 cycles with a radius of curvature of 4 mm.



Fig.1. Schematic diagram of the MTO/Ag/MTO/PDMS/MTO multilayer film in the unetched region ( $R_2$ ) and the PDMS/MTO/PET film in the etched region ( $R_1$ ).

### P07: Wearable Piezo Haptic Matrix - PHM

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Design and realisation of synthetic haptic aids to support the audio-visual communication is not an easy task. Especial challenge relies in designing wearable, non-intrusive well perceived systems with haptic feedback. The current paper describes a new wearable haptic device based on a matrix of nine piezoelectric actuators (3x3 Piezo Haptic Matrix - PHM). The device is made of 9 piezo actuators under independent control for stimulation at the forearm. The piezo actuators are bi-morph type with very fast response time (in micro-second range) are giving a ground for very wide range of haptic patterns to be synthesized. To drive and program the PHM we developed our own miniaturised driving electronics in very compact form. We implemented Particle Photon controller (with ARM Cortex M3 microcontroller) having full WiFi and Bluetooth connectivity which enabled wireless access and over-the-air programming possibility for numerous haptic experiments. The PHM platform is equipped with two ways of synthesizing haptic patterns; by using its internal digital programming (with Arduino-based language) and by exploiting an external arbitrary analogue signal. The internal programming relies on exploiting generic Arduino functions for signal generational, timing and stimulating process control. Utilising of an external analogue signal and function gives a way that any meaningful external input can be used to synthesise haptic patterns and trigger haptic perceptions on the user skin (such as microphone, camera, mobile phone, GPS module, music, natural sounds, human physiological signals, heartbeat, etc...)

The PHM offers possibility for a broad design of haptic patterns by varying basic frequency, waveform of stimulation, amplitude, and spatial location to make characteristic unique tactile codes. The strategy for mapping the haptic patterns has been investigated and a stroke based haptic sequential stimulation was selected as the most interesting one. The haptic-strokes were in favour because of great potential for covering haptic patterns related to numerous worldwide calligraphies (Asian, Chinese, European alphabets) by using haptic vectors and strokes delivered on user skin.



Piezo Haptic Matrix platform with full programmability and arbitrary signal input for synthesising haptic patterns

### P08: Novel 2-Micrometer Ag-Coated Cu Materials for High-Speed Die-Attach at below 250 °C

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Ag-finish dies were attached on Ag-finish substrates through sinter-bonding at below 250 °C using 2-micrometer Ag-coated Cu particles for attaining the bondline which do not melt or can sustain mechanical stability even at the temperature exceeding 300 °C, alike solder alloys.[1] The average thicknesses of Ag shell were 108 and 256 nm for 20 and 40 wt% Ag coated Cu particles, respectively. After mixing with  $\alpha$ -terpineol, the particles were printed on the substrate. The Ag shells were dewetted by instability at the interface of Ag layer/Cu core during heating for the die-attach, which is beneficial for the sinter-bonding. Thus, the sinter-bonding speed was outstandingly faster than that of pure Ag or Cu particles, even though nanoparticles were added in usage of the pure particles. Consequently, high shear strengths of 29.5-30.5 MPa and 35.6-36.3 MPa were measured even after short bonding for 0.5-1 min at 220 and 250 °C, respectively. Furthermore, significantly dense microstructure in the bondline was observed after the bonding for 5 min at both at 220 and 250 °C, which presenting more enhanced shear strengths of 55.2 and 68.4 MPa.



Fig1. Cross-sectional back-scattered electron images showing upper and lower bondlines of Ag-finished dies sinter-bonded at 220 °C using 40 wt% Ag-coated Cu particles for (a) 0.5, (b) 1, (c) 5, and (d) 10 min.

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# P09: Advanced nanostructured carbon/flexible polymer composites for multifunctional sensing

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Different polymer matrices (polyisoprene, ethylene-vinyl acetate etc.) and various electroconductive nanosized carbon allotropes (carbon black (CB), carbon nanotubes) were used to elaborate composites for multifunctional sensing. The carbon allotrope fillers were used in two ways – as one separate allotrope, and as two allotrope mix (hybrid). An attempt to increase the performance of chemical sensing was made by aligning of the conductive nanoparticles in liquid matrix using DC as well as AC electric field (Figure 1a).

The obtained polymer/nanostructured carbon composites (PNCC) possess piezoresistivity. The composites showed positive pressure coefficient of resistance – the resistance increases with increasing compressive force. By combining separate layers of PNCC in specific structure a sample with negative pressure coefficient of resistance (when the resistance decreases with increasing compressive force) was elaborated.

For the first time uncommon piezopermittivity effect was found – the real part of permittivity of PNCC noticeably decreases as pressure is applied (Figure 1b). A supercapacitor that was elaborated using porous PNCC as electrodes for the first time was tested as a pressure indicator and an enhanced piezopermittivity effect was found. In the latter case, as pressure was applied, the permittivity increased.

Planar design PNCC responds to concentration changes of volatile organic compounds (Figure 1a) as well as humidity changes in surrounding environment.

Triboelectric nanogenerators with PNCC components were also elaborated and tested as pressure indicators, where the mechanical vibrations induce the periodical voltage changes.

The PNCC with positive temperature coefficient showed photothermal response to laser radiation – the electrical resistance changed in opposite way compared to common semiconductor photodetectors. The mechanism of each sensing effect is explained basing

mainly on quantum charge tunneling effect between adjacent nanoparticles in percolative conductive channel structure inside the polymer matrix.



Fig1. (a) Ethylene-vinyl acetate/CB composite response elaborated using AC field (E=60 V/cm) tested in 500 ppm toluene vapor. (b) Piezopermitivity effect of polyisoprene/CB composites.

# P10: Effect of Mechanical Fatigue on Flexible Lithium Ion Battery for Wearable Electronics Applications

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To ensure reliable use of flexible lithium-ion polymer batteries for wearable electronics applications, the effects of mechanical fatigue on battery performance and safety have been important issues [1, 2]. In this investigation, the effects of fatigue deformation of a thin flexible lithium polymer battery on its capacity degradation, the state-of-health (SOH), and safety were studied. Fatigue test was performed as a function of strain mode (i.e., bending, torsion, and complex strain) and degree of strain up to 100,000 cycles. Charge/discharge cyclic test, electrochemical impedance spectroscopy (EIS), microstructural observation of

the dissembled battery components (i.e., anode, cathode, separator), and stress analysis by finite element method (FEM) were performed. As presented in Fig. 1, the mechanical fatigue at various degrees of strain accelerated capacity fade of the battery. The total electrochemical impedance value determined by EIS test was observed to be inversely proportional to the SOH value of the fatigued battery. Lithium precipitation was observed on the graphite electrode of the fatigued battery, while no such microstructural damage occurred for the as-received one. This needle-like metal precipitate caused puncturing of the polymer separator in the fatigued battery. Root causes of the battery degradation were discussed based on the microstructural analysis of the disassembled battery components. Approaches to retard the degradation caused by mechanical fatigue were suggested.



Fig.1. Capacity fade curve and EIS spectrum of the mechanically fatigued flexible lithium polymer batteries.

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### P11: Effect of Mechanical Fatigue on the Functional Degradation of Flexible Transparent Conductive Ag-nanowire Film

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Degradation mechanisms of the AgNW film under various mechanical fatigue conditions and their effects on electrical resistance and optical transmittance were investigated. Electrical resistance was measured in-situ during mechanical fatigue of folding and torsional strain conditions up to 100,000 cycles. Microstructural damage of the AgNW including welding of network junction, nanocracking, and fragmentation were observed for the fatigued films. Electrical resistance was observed to decrease initially before gradual increase with folding fatigue cycle. These changing tendencies were attributed to formation of welded junction and fragmentation of the AgNW, respectively. Increases in electrical resistance with folding degree and cycle were caused by nanocracking and fragmentation of the AgNW under torsional fatigue condition. Structural damages of the AgNW including welded junction, nanocrack, as well as fragmentation caused by mechanical fatigue stress do not degrade optical transmittance of the AgNW film.



Fig. 1 Change in electrical resistance of the Ag-nanowire coated film under various mechanical fatigue conditions.

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