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Sustainable Energy Applications Performed by the Duo-Plasmaline Microwave Plasma Source and the Plasma Array

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1 Introduction – Characteristics of Low-pressure Microwave Plasmas

Microwave plasma excitation at low-pressure conditions is based on acceleration of free electrons in the electric field of the microwave. Heavy charged particles such as ions are not able to follow the fast changing polarity of the electric field of the microwave in the GHz range due to inertia and virtually remain at their original energy level, which is generally correlated with ambient temperature. By collisions of accelerated free electrons with electrons from the shell of neutral atoms or molecules and charged ions, respectively, kinetic energy of these accelerated free electrons will be transferred to the shell electrons. Consequently, shell electrons will be excited or even overcome the attractive force of the nucleus, and bonding electrons in molecules can be separated. This leads to emission of light characteristic for the element or molecule when the shell electron falls back from the excited state into its original energy state, to the generation of additional free electrons as well as positively charged ions and to the formation of radicals in the latter case, respectively. The exponential generation of additional free electrons – the so-called avalanche effect – is causal for the formation of a plasma, characterized by a significant ratio of ionization of the gas particles and a correspondingly high density of free electrons.

The pressure is another important parameter for the characteristics of the microwave plasma, since the pressure directly correlates with the collision frequency of the free electrons. At low-pressure conditions and the mean free path of the accelerated free electrons being significantly shorter than the dimensions of the vacuum chamber, a non-equilibrium plasma is formed, characterized by neutrals and ions at ambient temperature and by “hot” accelerated free electrons. When the pressure

in the vacuum chamber is reduced so that the mean free path of the free electrons is in the range of the dimensions of the vacuum chamber, the probability of collisions of the free electrons with the walls of the vacuum chamber significantly increase, thus inhibiting the avalanche effect which is essential for forming and sustaining a plasma. Increasing the pressure will allow energy transfer to heavy particles like neutrals and ions, too, causing the plasma to gradually thermalize. Thus, the gas temperature of the plasma increases, too. In addition, when keeping the microwave energy constant by increasing particle density, the excitation energy will not be sufficient to maintain the plasma volume, which results in the formation of plasma filaments.

Increasing electron density at constant pressure finally inhibits the propagation of the microwave. At the so-called critical density, the electromagnetic wave can no longer penetrate the plasma and is reflected. The plasma then acts like a conducting wall. The critical density is proportional to the square of the frequency of the electromagnetic wave.

Based on these principles, many technical microwave plasma sources have been realized to exploit the high reactivity of microwave plasmas due to the high density of radicals. However, the formation of specific modes and of standing waves, respectively, according to the vacuum wavelength of the microwave, which is in the same geometrical dimension as the material to be treated, can lead to inhomogeneous plasma treatment of the surface of the this material. Easy upscaling of microwave plasma sources for plasma treatment of large substrates is another challenge. The Duo-Plasmaline microwave plasma source as well as the plasma array, which is based on the Duo-Plasmaline, perfectly meet these challenges.

2 Duo-Plasmaline and Plasma Array Low-pressure Microwave Plasma Sources

2.1 Duo-Plasmaline

The Duo-Plasmaline is a low-pressure microwave plasma source. The plasma is formed by microwave excitation only, i.e. without the effect of an additional magnetic field. In a simplified description, the Duo-Plasmaline is like an inverse fluorescent tube excited by microwaves: a coaxial line is mounted through the vacuum vessel (i.e. the process chamber) made of electrically conducting material and powered by microwaves from both sides. Inside the vacuum vessel, the outer coaxial conductor is replaced by a dielectric tube made of e.g. glass, quartz or ceramics. The inside of the dielectric tube is at atmospheric pressure (for proper cooling of the antenna), whereas the outside (i.e. the process chamber) is at low pressure, preferably in the range between 10 Pa and 1000 Pa (the pressure is defined by the related application, i.e. etch, deposition etc.). Microwaves can pass the dielectric tube and propagate into the low-pressure regime of the vacuum vessel. When the electric field strength of the microwave exceeds the breakdown field strength, a discharge ignites in the low-pressure regime at both ends of the Duo-Plasmaline where the outer coaxial conductor is replaced by the dielectric tube. The short plasma hoses formed at both ends of the Duo-Plasmaline are electrically conducting media and thus replace the missing outer coaxial conductor. With increasing microwave power, the plasma extends from both ends alongside the dielectric tube, until an axially homogeneous plasma is finally formed (see Figure 1).



Figure 1: Axially homogeneous plasma formed around the Duo-Plasmaline low-pressure microwave plasma source [1].

The formation of an axially homogeneous low-pressure plasma around a Duo-Plasmaline with a length of more than 3 m has been demonstrated by

application of only some kW of microwave power at the frequency of 2.45 GHz.

2.2 Plasma Array

A two-dimensional plasma array is obtained when arranging two or more Duo-Plasmalines equidistantly and in parallel. While a Duo-Plasmaline provides an axially homogeneous plasma, a large homogeneous plasma can be formed by a plasma array (see Figure 2). Consequently, a Duo-Plasmaline is preferably used for plasma surface treatment in continuous in-line processes, whereas a plasma array is suitable for continuous and batch processes, respectively. Both Duo-Plasmaline and plasma array provide highly efficient surface treatment of even thermally sensitive materials due to high radical densities at simultaneously low ion energy of the non-equilibrium microwave plasma at low-pressure.

Their modular design makes it easy to adapt plasma arrays to the dimensions of the material to be treated in a plasma surface process by configuring the number and the length of the Duo-Plasmalines in the plasma array. In this way, the active plasma area can be scaled both in width and length.

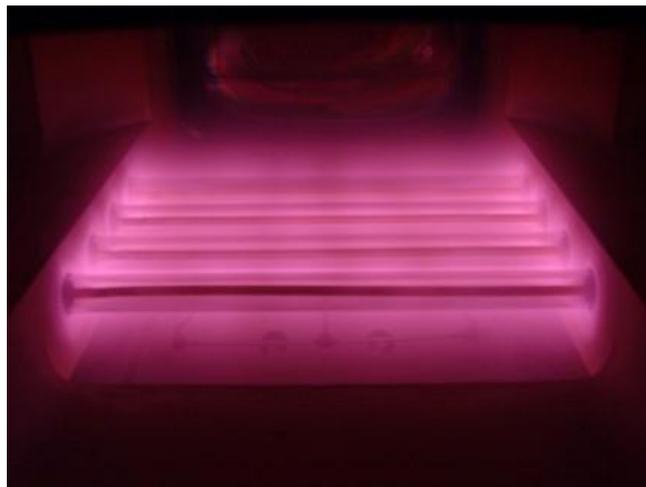


Figure 2: Two-dimensional homogeneous plasma formed by a plasma array microwave plasma source at low-pressure conditions [2].

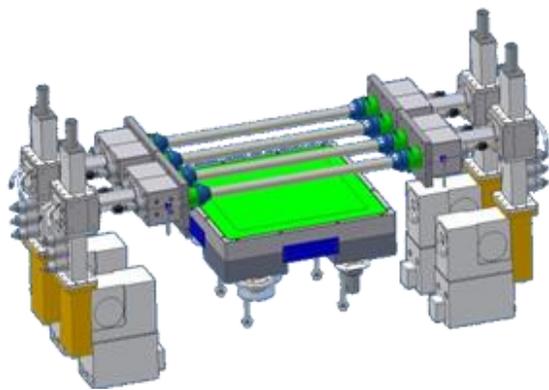


Figure 3: Schematic of a plasma array consisting of four Duo-Plasmalines (including magnetron head, tuner and isolator, power supply is not shown) for plasma treatment of the green surface below at low-pressure conditions.

A schematic of a plasma array consisting of four Duo-Plasmalines in a process chamber for plasma surface treatment at low-pressure conditions is shown in the Figure 3. The four Duo-Plasmalines are supplied with microwave energy from the left and from the right. The microwave energy is generated by two magnetrons on each side. Each magnetron supplies two Duo-Plasmalines via power splitter with microwave energy. Splitting microwave power equally to two or more Duo-Plasmalines provides for increased homogeneity of the plasma area formed by the plasma array. Figure 4 shows a plasma array consisting of six Duo-Plasmalines with a length of 160 cm each, thus forming an active plasma area of approximately 150 cm x 200 cm for e.g. coating of solar cells with silicon nitride films. In general, the size of the active plasma area can vary from a fraction of a square meter to a few hundred square meters.



Figure 4: Plasma array consisting of six Duo-Plasmalines integrated into a process chamber for e.g. low-pressure plasma deposition of thin films used in the production of solar cells (courtesy of Meyer Burger Germany).

Apart from deposition of thin films, Duo-Plasmalines and plasma arrays are also used for

plasma assisted surface treatment like surface activation, etching, cleaning and even sterilization.

3 Examples for Sustainable Energy Applications Performed by the Duo-Plasmaline Microwave Plasma Source and the Plasma Array

3.1 Plasma Deposition of Anode Materials for Lithium-ion Battery Applications

In 2007, researchers at Stanford University discovered a solution to the challenges associated with silicon in batteries. They were able to store lithium in tiny silicon nanowires by using new techniques and methods from nanotechnology. The dimensions of these silicon nanowires are about one thousand times thinner than the thickness of a sheet of paper. The silicon nanowires are able to swell when they take-up lithium, while physical effects on nanoscale inhibit the silicon from fracturing and breaking apart.

Therefore, silicon is widely considered to be the future material of choice in anode technology – battery-builders and automakers are working on ways to take advantage of its high theoretical charge capacity. Batteries with silicon anodes achieve significantly higher energies per unit volume and per unit weight than today's commercially available batteries based on carbon-anode designs.

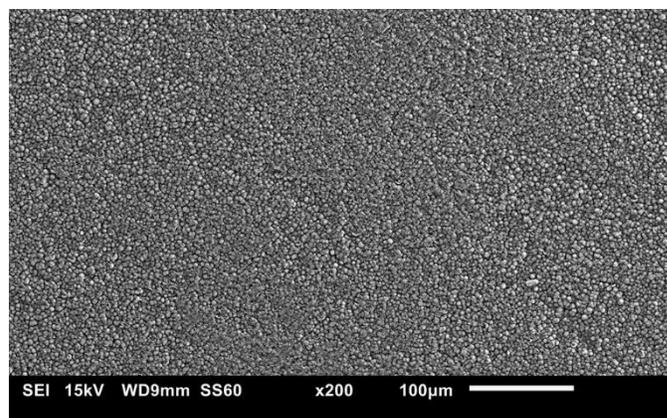


Figure 5: Three-dimensional growth of silicon columns by low-pressure microwave plasma deposition for pure silicon anodes [3].

Manufacturing facilities relying on Duo-Plasmaline technology for plasma enhanced chemical vapor deposition (PECVD) of three-dimensional porous silicon layers have the potential for producing silicon nanowire anodes. Figure 5

shows silicon columns three-dimensionally grown by low-pressure microwave plasma deposition for pure silicon anodes.

3.2 Plasma Deposition of Silicon Nitride for Photovoltaic and Semiconductor Applications

Thin films of silicon nitride (SiN) are widely used in microelectronics, optoelectronics, optics and hard surface coatings. Figure 6 shows a thin plasma-polymerized SiN film on a silicon wafer used in microelectronics. This SiN film was deposited in a low-pressure plasma deposition process by application of a microwave-powered plasma array.



Figure 6: SiN film plasma deposited in a low-pressure plasma deposition process on a silicon wafer by application of a microwave-powered plasma array [4].

Effective silicon solar cells require minimal reflection losses and minimized surface recombination. Thin plasma-polymerized SiN films are used to minimize both properties, the reflection behavior by adjusting the refractive index of the anti-reflection coating and the surface properties to avoid recombination at and near to the surface.

Their hardness and chemical resistivity are further advantages of SiN films. For this reason, they can be applied as insulator material and barrier layer in many industrial applications, too.

3.3 Plasma Deposition of Barrier Layers for Photovoltaic Applications

Today, application of photovoltaic devices is an economical means for producing green electrical energy. However, photovoltaic devices will be more profitable if their price can be significantly reduced, e.g. by large-scale production. Thin film solar cells

are of particular interest regarding large-scale production. Glass plates are state-of-the-art substrates for thin film solar modules made of e.g. copper indium gallium di-selenide (CIGS). They can be replaced by thin metal foils to reduce weight as well as material costs. Standard CIGS solar modules consist of monolithically connected solar cells. Therefore, the metal foil has to be insulated. In addition, diffusion of material impurities and of material elements from the metal foil into the CIGS must be prevented by a diffusion barrier, too. However, there are also some advantages when using thin metal foils as substrate material: they provide new flexibility to the modules, making them suitable for mobile applications and other niche domains.

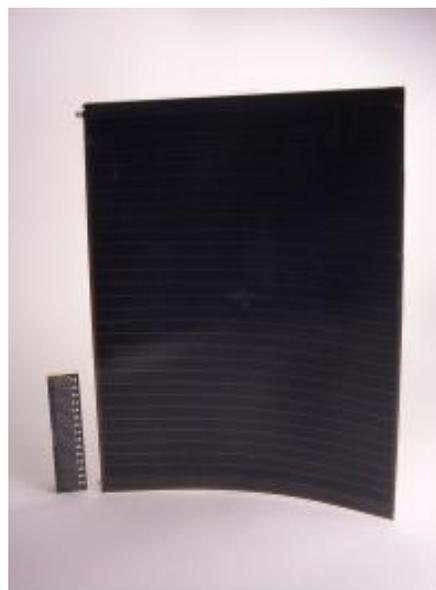


Figure 7: Monolithically connected copper indium gallium di-selenide (CIGS) solar modules on a flexible metal foil with a plasma-deposited diffusion layer in between [5-7].

The glass substrate (as well as the glass covering) can be replaced by a systems of thin polymer films deposited in a low-pressure microwave sustained plasma process on the metal plate (and on the optical layers on top of the CIGS solar modules, respectively). A monolithically connected copper indium gallium di-selenide (CIGS) solar modules on a flexible metal foil with a plasma-deposited diffusion layer in between is shown in Figure 7. These plasma processes for deposition of thin polymer films acting as diffusion barriers establish new technologies for economical production of flexible photovoltaic modules.

Furthermore, plasma processes can be used for deposition of thin film amorphous silicon (a-Si) solar cells and microcrystalline silicon ($\mu\text{c-Si}$) solar cells, too, thus providing important new markets for plasma technology.

3.4 Plasma Surface Modification and Activation for Applications in Fuel Cell Technology

Fuel cells based on ionomer membranes are very important e.g. for zero emission vehicles. The major disadvantage of commercially available membranes such as Nafion in direct methanol fuel cells (DMFC) is their relatively large permeability of methanol, which leads to a drastic degradation of the efficiency of the fuel cell. Figure 8 shows the schematic of a DMFC. Plasma surface treatment of such membranes can reduce the permeability of methanol. In addition, the bond strength of the membrane to the catalyst can be improved by plasma surface treatment.

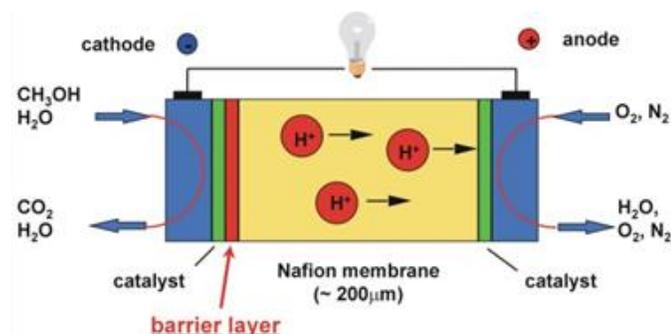


Figure 8: Schematic of a direct methanol fuel cell (DMFC) [8-9].

The porous gas diffusion layer (GDL) is another important component of a fuel cell. It provides a homogeneous gas flow to the catalyst and controls the water content of the cell. In particular, the water management in a wide range of the voltage/current polarization curves of the fuel cell is very important for the efficiency of the fuel cell. However, GDLs mostly consist of a strongly hydrophobic material which is critical for a proper water management. A partially hydrophilic GDL is a better choice, because it can retain a certain amount of water in the fuel cell.

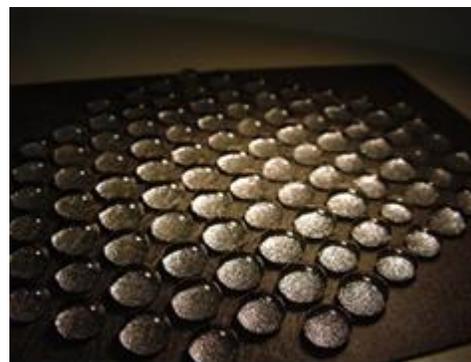


Figure 9: Originally completely hydrophobic surface of a gas diffusion layer (GDL), showing hydrophilic properties on the areas exposed to the plasma (cf. water droplets adhered to these hydrophilic areas after low-pressure microwave plasma treatment) [9-10].

Partially hydrophilic properties of the GDL can be achieved by a surface treatment of the GDL in a nitrogen plasma process for example. When the GDL is covered by a perforated plate, only the uncovered areas of the surface of the GDL will be modified in the plasma process. Consequently, the uncovered areas of the surface of the GDL show hydrophilic properties after plasma treatment (cf. the water droplets adhering to these areas in Figure 9), whereas the covered areas of the surface of the GDL retain their hydrophobic properties. The fuel cell with plasma treated GDL shows significantly higher cell voltages than the reference fuel cell without plasma treated GDL. This is due to the fact that the membrane of a fuel cell without plasma treated GDL runs dry, especially at higher current densities. When using a plasma treated GDL, a certain amount of water can be retained in the cell leading to a better fuel cell performance.

4 Summary

Today and even more in future, there are and there will be many different applications of surface modification by low-pressure microwave plasma processes in the field of sustainable energy production and storage. The examples presented for deposition of silicon nanowires for novel lithium-ion batteries, for deposition of silicon nitride films and of polymer-based diffusion barriers for photovoltaic and semiconductor applications as well as for surface modification in fuel cell technology require non-equilibrium microwave plasma processes at low-pressure conditions. High radical densities,

homogeneity of the plasma on a large area as well as easy upscaling are major characteristics of these non-equilibrium microwave plasmas at low-pressure conditions, which can be easily generated by the Duo-Plasmaline microwave plasma source and by the plasma array based on the Duo-Plasmaline.

For further readings

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About the Author



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Microwave Assisted Bulk Production of High-quality Reduced Graphene Oxide for Battery Applications*

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***A brief account on the recent paper (an open access article under CC BY 4.0 License) published by Loughborough's Advanced Ceramics Group [9]**

Rapid production of high-quality reduced graphene oxide (rGO) with less oxygen functional groups (OFGs) and large lateral dimensions is pursued

worldwide owing to the fascinating intrinsic properties of graphene such as highly flexible but mechanically robust structure, excellent electronic

conductivity, and massive theoretical specific surface area [1, 2]. High-quality rGO has found widespread applications in energy generation/storage devices, especially Li-ion batteries, LIBs [3-5]. Although chemical vapor deposition (CVD) and mechanical exfoliation approaches have been well developed to produce graphene-based products, their outcomes are generally unsatisfactory due to the high cost and the tedious process involved. The alternative approach to produce graphene is reduction of GO using chemical reducing agents or conventional thermal treatment. Nevertheless, the synthesized rGO possesses high concentration of OFGs and low carbon-to-oxygen atomic ratio (C/O). In order to produce high-quality rGO in a rapid and low-cost manner, reduction of GO using microwave irradiation is recently explored because it simultaneously combines the advantages of low cost by Hummer's method and super-fast volumetric heating by microwave irradiation [6-8]. Further, despite the commercial success of LIBs as power sources for portable electronic devices, the commonly used graphite anode and LiCoO₂-based cathode cannot satisfy the demanding requirements of the advanced LIBs due to the low capacity and the inferior rate capability, respectively. Therefore, it is envisaged that the electrochemical properties of LIBs can be improved significantly using high quality microwave processed rGO (MWrGO) because it is regarded as a promising electroactive material to replace traditional graphite in anode and as a conductive additive in cathode. Thus, the twin objectives of this study [9] were to rapidly produce high quality rGO via microwave treatment of GO in the solid state and assess the performance of MWrGO for battery anode and cathode applications.

In this work [9], the GO prepared using the modified Hummer's method was first pre-annealed at 250 °C to restore partial graphitic structures before being subjected to microwave irradiation at different powers (300, 500, and 800 W). The microwave-synthesized products of annealed GO are denoted as MWrGO-X where X represents the microwave power. It is found that the microwave-assisted reduction process can be completed within few seconds at the super-fast heating rate of 30,000 °C/min. For comparative study of the impact of pre-annealing treatment on microwave absorption,

GO without pre-annealing treatment (denoted as unannealed GO) was subjected to microwave irradiation and was compared with annealed GO. Detailed computer simulation using reactive molecular dynamics (RMD) was used to mimic the thermal deoxygenation process of OFGs at different microwave powers by considering the microwave localized heating of functionalized carbon atoms. The simulation results suggested that different microwave powers could be used to tailor the quality of MWrGO – a unique trait that can be exploited based on need. The obtained MWrGO-800W exhibited a highly porous structure, high C/O ratio (≈ 14.29), high surface area (310.24 m²/g) and high electronic conductivity (761.4 S/m). For LIBs application, the anode made of MWrGO-800W delivered a high discharge capacity of 750.0 mAh/g at 0.2 A/g with near-zero capacity loss after 100 cycles. Additionally, the LCO-based cathode with MWrGO-800W as conductive additive was shown to exhibit an improved capacity retention and rate capability compared to the counterpart containing carbon nanotube (CNT) or graphite.

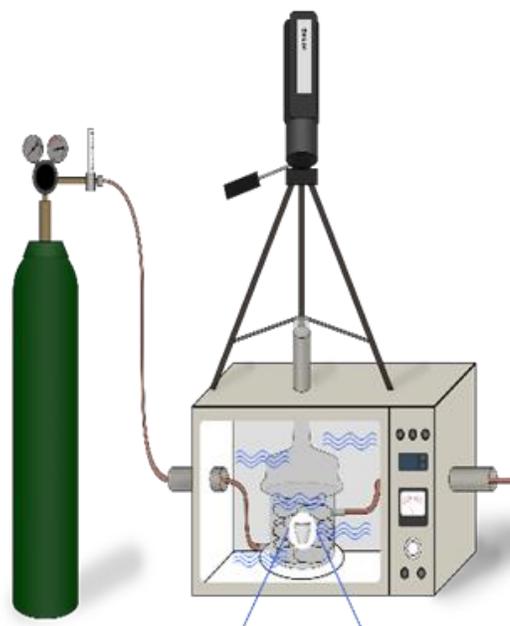


Figure 1: Schematic of the microwave set-up used for reduced graphene oxide production. AR gas was used for creating an inert atmosphere [9].

The as-prepared GO was annealed at 250 °C for 1 hour in argon atmosphere to obtain annealed GO. The annealed and unannealed (as-prepared) GO was placed inside a microwave transparent quartz

reactor, which was flushed with argon gas for 10 min to create an inert atmosphere. Microwave irradiation was performed at powers of 300, 500, and 800 W using a customized microwave oven (Fig. 1) operating at 2.45 GHz frequency. For comparison, as-prepared GO without the annealing treatment (denoted as unannealed GO) was exposed to 800 W microwave irradiation in identical argon atmosphere. Upon microwave irradiation, the real-time temperature profiles across annealed GO and unannealed GO were monitored (Fig. 2) using thermal imaging camera (FLIR-A655sc, Sweden).

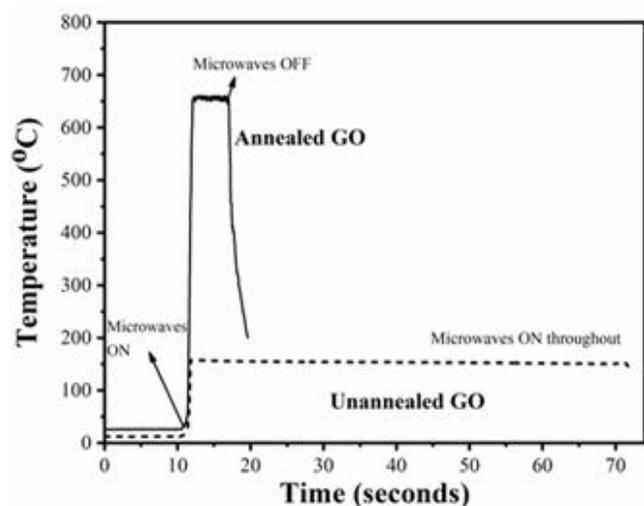


Figure 2: Time-temperature profiles of annealed and unannealed GO by 800 W microwave irradiation. The heating rate observed is $\sim 30,000$ °C/min for annealed GO and ~ 2000 °C/min for unannealed GO [9].

Fig. 2 depicts the effect of pre-annealing treatment on the microwave absorption of unannealed GO and annealed GO. The annealed GO could be heated up to ~ 670 °C within few milliseconds due to the boosted microwave coupling capability caused by partial restoration of conjugated graphitic structure. This is in sharp contrast with the highest temperature of only ~ 160 °C achieved on the unannealed GO. The modified Hummer's method introduced OFGs on the basal planes of GO, which cleaved the defect-free conjugated structure down to tiny polyaromatic islands [3]. Those polyaromatic islands created inter-boundaries along the vicinity of the OFGs and thus confined the transportation of π electrons within delimited regions. Consequently, the π electrons were hard to be driven by the E-field component of the electromagnetic microwaves to

transport over a long range to generate enough Joule heating to effectively reduce GO. Fortunately, GO is thermodynamically unstable due to the incorporated -OH and -C=O groups [3]. The pre-annealing treatment of GO at 250 °C can remove the -OH and -C=O groups and thus eliminate the inter-boundaries of defective regions, leading to partial restoration of the conjugated structures. This enabled the transportation of π electrons over a longer distance and generated significant amounts of Joule heating, yielding a remarkable heating rate of 30,000 °C/min for annealed GO. This value was far greater than that of 2,000 °C/min achieved in conventional rapid thermal reduction method [10]. This superfast heating rate was the direct result of intense microwave absorption and efficient conversion from microwave energy to thermal energy [10]. Furthermore, the obtained high temperature (~ 670 °C) of annealed GO was also believed to result in the localized deoxygenation of OFGs. The pristine quality of the MWrGO was confirmed by high resolution TEM, selected area electron diffraction (SAED) and micro-RAMAN spectroscopy [9].

It is also interesting to find that during microwave processing strong arcing was observed on annealed GO after just 1-3 s of microwave irradiation (Fig. 3), whereas no arcing was observed on unannealed GO even after even 60 s of exposure. The occurrence of microwave induced arcing may be ascribed to the congregation of π electrons at the sharp sites on graphene planes, which led to the ionization of the surrounding gas [11]. During microwave irradiation of annealed GO, the residual OFGs were locally heated and deoxygenated, which further eliminated the inter-boundaries around OFGs and enabled more π electrons to transport over a longer distance. In this scenario, a higher concentration of π electrons was built up at sharp sites, such as plane edges or defective points, resulting in the formation of intense electrostatic field [12]. The induced electrostatic field was likely to ionize the surrounding gas through electron excitation, which was perceived as electric arcing. It is also believed that the microwave reduction of GO was a self-accelerating deoxygenation process because the freshly formed MWrGO themselves became additional microwave absorption regions and in turn converted more microwave energy to thermal energy to remove the residual OFGs.

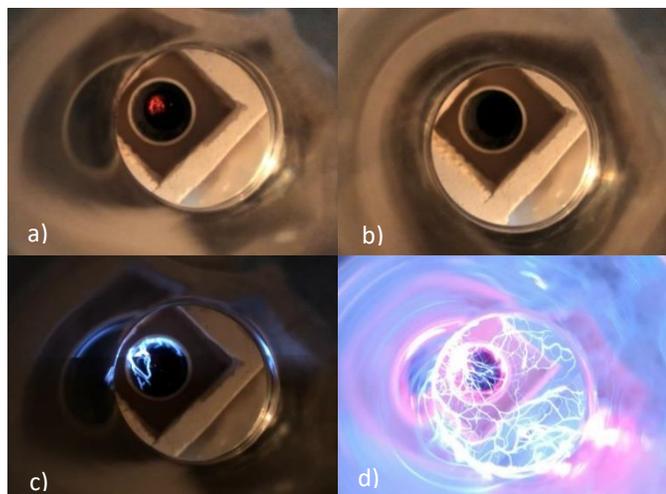


Figure 3: Thermal images of the occurrence of arcing during microwave irradiation on annealed GO. (a) Before microwave irradiation, (b) Heating up of GO samples at the beginning of microwave irradiation, (c) The initiation of arcing from GO surface, and (d) the development of intense arcing with extended microwave exposure [9].

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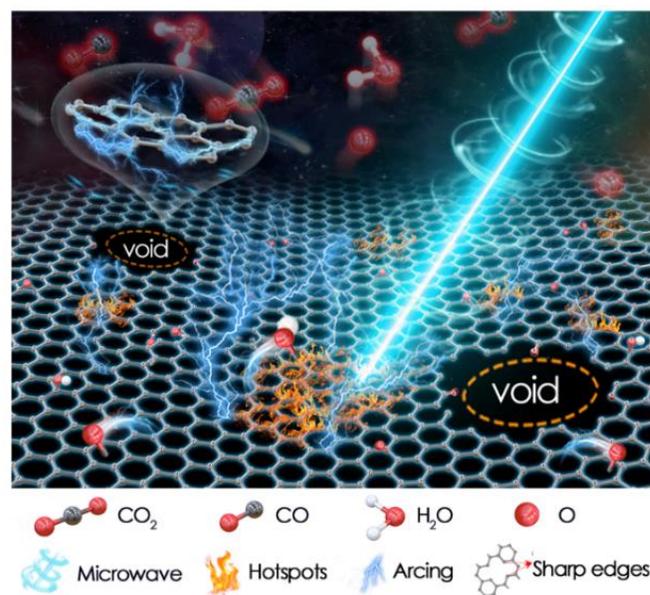


Figure 4: Mechanistic aspects of microwave interaction on annealed GO: The microwaves are absorbed by oxygen functional groups and resulted in localized overheating, which lead to the formation of hotspots. The high temperature of hotspots can effectively deoxygenate the oxygen functional groups, thereby resulting in the release of gaseous species (CO_2 , H_2O , CO and O) and the formation of structural voids on the graphitic backbone. During microwave irradiation, the E-field component of the electromagnetic microwaves drive the π electrons to accumulate at the sharp edges of voids of the graphene planes. This leads to the ionization of surrounding gas and the occurrence of intense arcing [9].

MD simulation has provided useful insights into the atomistic information regarding transformations and deoxygenation of OFGs during microwave irradiation. Two simulation scenarios, i.e. direct heating and microwave localized heating, were carried out. From the simulation results, it was concluded that the hydroxyl groups were decomposed from GO sheets at roughly 1200 K, followed by removal of epoxide, and carbonyl groups above 2200 K. The decomposition of hydroxyl groups at lower temperature was supported by previous research [13, 14]. Based on the simulation results, the decomposition mechanisms of hydroxyl, epoxide, and carbonyl groups are proposed (Fig 4). The hydroxyl group was decomposed from carbon skeleton by breaking the C-OH bond during microwave irradiation and then was released as a hydroxyl free radical. As for the decomposition of epoxide group, the two C-O bonds sequentially broke, and an oxygen atom was then released, as

illustrated. Notably, if two epoxide groups are linked by a carbon-carbon bond, they tended to transform into a pair of carbonyl groups as shown, which was also reported by Abolfath [15]. With regard to the paired carbonyl groups, one carbonyl group was rearranged with the C-CO bond of another carbonyl group and became an over-coordinated epoxide group, releasing a CO molecule.

Battery anode and cathode structures were prepared and electrochemically characterized using the approaches described elsewhere [9]. For anode, the slurry of 60 wt% MWrGO and 40 wt% polyvinylidene fluoride (PVDF) was prepared using N-methyl pyrrolidinone (NMP, 99%) and was blade cast on Cu foils, followed by drying at 100 °C overnight. Afterwards, the dried electrode was roll pressed and punched out (8 mm discs). The mass loading was ~ 0.2 mg/cm². For cathode, the stoichiometric amounts of Co₃O₄ ($\geq 99\%$, Sigma) and Li₂CO₃ ($\geq 99\%$, Fisher) were first ball milled at 200 rpm for 16 hours with the ball-to-powder ratio of 10:1, followed by calcination at 850 °C for 5 hours to prepare LiCoO₂ (LCO). The slurry of 91% LCO, 1 wt% MWrGO-800W and 8 wt% PVDF was prepared for MWrGO-containing cathode (LCO-MWrGO) and the slurry of 89 % LCO, 3 wt% CNT and 8 wt% PVDF was prepared for CNT-containing cathode (LCO-CNT) using NMP. The slurries were blade cast on Al foils, followed by drying at 100 °C overnight. Afterwards, the dried electrodes were roll pressed and punched out (8 mm discs). The mass loading was ~ 3.1 mg/cm² for LCO-MWrGO and ~ 3.0 mg/cm² for LCO-CNT.

All the working electrodes prepared above were assembled in 2032 type coin cells with lithium metal as counter electrode in Ar-filled glove box (MBraun). Celgard 2325 membrane was used as separators and the electrolyte of 1.0 M LiPF₆ in ethylene carbonate/dimethyl carbonate (1:1 v/v) was used. All the cells were conditioned for 1 day and galvanostatically charged/discharged using multi-channel battery tester (Neware, BTS-4008). For battery (LIB) applications, the anode made of MWrGO-800W was demonstrated to deliver a high capacity of ~ 750.0 mAh/g with near-zero capacity loss after 100 cycles [9]. Additionally, a highly conductive 3D network constructed by porous MWrGO-800W provided LiCoO₂ with a high-capacity retention of $\sim 70\%$ at the high current rate of

10 C, which is promising for power-oriented cathode.

Hence (i) it is demonstrated that by incorporating a preliminary step of converting graphene oxide (GO) from a poor microwave (MW) absorber to an excellent microwave absorber through a simple pre-annealing treatment, the reduction process of GO can be fully accomplished using microwaves at an ultra-fast heating rate of 30,000 °C/min to produce high quality microwave reduced graphene oxide (MWrGO) in bulk; (ii) Reactive molecular dynamics simulations provided significant insights into the molecular-level interaction of annealed GO with microwaves and suggested that a relatively low-power (800W – something that is commonly available) microwave irradiation resulted in efficient removal of oxygen functional groups and the formation of structural voids on the graphene plane through localised heating. The E-field component of the microwaves drive the π electrons to accumulate at the sharp edges of voids of the graphene planes leading to the ionization of surrounding gas and correlates the observed occurrence of ‘arcing’; and (iii) For battery applications, the anode made of MWrGO-800W delivered a high capacity of ~ 750.0 mAh/g with near-zero capacity loss after 100 cycles. Additionally, a highly conductive 3D network constructed by MWrGO-800W was found suitable for a power-oriented cathode.

Thus, the microwave-assisted reduction of GO provides a rapid way to produce high-quality reduced graphene oxide for energy storage devices at an affordable cost and at bulk scale.

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Bala Vaidhyathan (Vaidhy) is a Professor of Advanced Materials and Processing and was the Associate Dean for Enterprise at the School of Aeronautical, Automotive, Chemical and Materials Engineering at Loughborough University (LU). He

leads the very active Advanced Ceramics Research Group in the Materials Department and has over 160 peer reviewed publications (>4270 citations, h-index 35), named inventor on 17 patents, delivered >50 Plenary/keynote/invited presentations in international and national conferences and written six book chapters. He is the Editor of *Advances in Applied Ceramics*, a high impact UK journal published by Taylor & Francis and on the Editorial Board for four International Materials Journals. He held/holds >45 research grants totaling >£12.2M in the last 10 years alone funded by EPSRC, Innovate UK, Royal Society, DSTL, Government/Charity organisations and many of these are with multi-partner, multi-institutional involvements and 38 of them had direct industrial steer and contribution. He is a member of ACerS, ECerS, ICS (life member), MRS, AMPERE, DCERN, IOM3 and is a Fellow of the IoN. He is also the fellow of Higher Education Academy, UK. He won numerous awards and prizes including the prestigious 'Glory of India' Award for his contribution to Science, Technology and Education in 2010 and Verulam Medal and Prize for his significant contributions to the field of ceramics by the Institute of Materials, Minerals and Mining (IOM3), UK in 2015 and the Pfeil Award for the best paper in the ceramics field in 2017. Vaidhyathan has pioneered the development of energy efficient microwave, flash and hybrid methods for the advanced processing of functional ceramic materials and Loughborough is currently regarded as one of the world leaders in the utilization of these techniques and hosts the largest nanoceramics group in UK. With over 20 years of experience, he is one of the leading exponents in the field of microwave-assisted materials manufacturing, additive manufacturing of advanced ceramics, pioneered the development of hybrid two stage sintering methods and was the first to set up an atmosphere controlled, gradient field assisted sintering facility for the processing of oxide and non-oxide materials and devices. The range of products worked on has been very wide, from traditional to nanostructured materials, for energy, electronic, defence and healthcare applications. LU Materials department is also the home of the Loughborough Materials Characterisation Centre (LMCC), a specialised facility for state-of-the-art materials characterisation in all length scales from surface to bulk, from microscopic to macroscopic structure determination and BV's team commands significant analytical expertise on structure-property correlations

Ricky's Afterthought:**Is Hydrogen from Renewable Energy the Solution to Decarbonisation?****A.C. (Ricky) Metaxas**

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The majority of the countries, with few exceptions, have agreed to abide by net zero CO₂ emissions by 2050 as agreed by the intergovernmental Panel on Climate change. These issues will be discussed in the COP26, the UN Climate Change Conference in Glasgow in November. COP stands for “Conference of the Parties” a decision-making body of the United Nations Framework Convention on Climate Change (UNFCCC).

Energy consumption accounts for about three quarters of all man-made greenhouse emissions. The biggest culprits include electricity generation and heat, transportation, manufacturing and construction. Each of these sectors is looking to specific ways of reducing their footprint by novel methods.

Recently there has been much reference in European government circles about the use of hydrogen as the fuel of the future as a replacement for natural gas particularly for meeting the stated goal of net zero by 2050.

Hydrogen is abundant and can be derived either from water via electrolysis or as a by-product of methane after blasting it with steam. The goal is to be able to produce green hydrogen at scale using renewables or clean hydrogen by CCS (Carbon Capture and Storage) to capture the CO₂ before it is emitted into the atmosphere. CCS can remove up to 90% of a power plant's CO₂ emissions by capturing it and transporting it to depleted oil and gas fields or in saline aquifer formations.

However, who is likely to benefit from a move to a hydrogen-driven economy?

Hydrogen use

Refineries are heavy users of hydrogen as it is used

to lower the sulphur content of petroleum, a process termed hydrodesulphurisation. Other uses include fuel in use in vehicles, in treating metals and in food production. The chemical industry is also a heavy user of hydrogen as it is important in the manufacture of ammonia which is inherent in the production of fertilisers. It is also used in the production of methanol which is used in the manufacture of many polymers.

Hydrogen production

Hydrogen can be readily produced by electrolysis of water by passing electricity through an electrolyser. If the latter is powered from excess renewable energy, such as wind or solar, the resulting hydrogen is termed green hydrogen. This process however is very expensive and would make the viability of hydrogen at present as a replacement for natural gas difficult to justify.

Alternatively, hydrogen is produced by steam reforming, that is, by blasting methane with steam to produce hydrogen and carbon monoxide, in the following process:



If in this process the waste is released to the atmosphere then the product is termed grey hydrogen whereas if the waste is captured and geologically stored (CCS) it is then called blue hydrogen.

Renewable energy

If green hydrogen is to be produced at scale we need to increase the installation of wind and solar PV farms which will produce electricity not only to

power our homes and industry but have excess renewable energy to manufacture hydrogen which in turn could be burned to produce electricity. Wind farms are very well established in the UK and the commitment is to have a capability of 40GW by 2030. Almost a quarter of the electricity generation in the UK in 2020 was from wind. Renewables rose to 38% of Europe's electricity to overtake fossil fuel electricity production which fell to 37%. Germany's power consumption in 2020 amounted to 46% from renewable energy, mainly wind and solar photovoltaic.

Hydrogen for power generation

Having produced hydrogen at scale it can then be used directly to produce electricity in 100% hydrogen fuelled power stations. In 2019 natural gas, predominantly methane, accounted for almost 39% of the UK's electricity production. Switching from methane to hydrogen in a power station is not a simple task. Hydrogen burns at different temperatures and at different speeds and the optimisation process, particularly the amount of oxygen it needs, requires careful consideration. Scottish and Southern Energy (SSE) in the UK is working with Equinor to produce a methane power station with CCS as well as the first 100% hydrogen fuelled power station at Keadby and Peterhead.

Home heating

Home heating is a big problem at present, using natural gas as it makes a huge contribution to the greenhouse gases which in the UK alone amounts to between a third and a quarter of the emissions. This is around 10 times more than the CO₂ created by the aviation industry.

It is understandable then why the giant energy companies, such as Shell and BP, are pushing hard the need to replace natural gas, that is methane, with hydrogen and use the existing distribution network. It would mean that their operations would continue and all they need to do in the case of home heating is to pump hydrogen to homes instead of natural gas. If this is to happen most of the metal pipes would have to be replaced because hydrogen reacts with the metal and makes it brittle. However, polyethylene pipes are much better for transporting hydrogen and this is in progress already at least in some parts of the

UK. Further, the size of the boiler used for home heating will be the same as existing natural gas boilers so the consumer will not notice much difference. The last thing that the energy giants wish to see is a conversion to electricity for heating our homes (such as using an air source heat pump to transfer heat from the outside air and transfer it internally to heat water which is piped to radiators) thus making their existing vast distribution network for natural gas redundant.

District heating

Another option for reducing CO₂ emissions is district heating where water is heated in a central facility using waste heat from industry or using renewables to heat it and have it pumped to homes using heavily insulated pipes. This is a massive undertaking if it is going to be adopted widely.

Green Hydrogen in Europe and the UK

A joint initiative between BP and Danish offshore wind farm Ørsted based at Fredericia has recently been announced that will generate 1 tonne per hour of green hydrogen using a 50 MW electrolyser using the farm's excess electricity. This will be able to replace grey hydrogen consumption at one of BP's refinery in Germany by 20% amounting to a saving of about 80000 tonnes of CO₂ equivalent emissions per annum. It is aimed eventually to use a 500 MW electrolyser in the refinery to produce renewable hydrogen and dispense with the current fossil fuel-based hydrogen thus improving dramatically their CO₂ footprint.

One of Europe's biggest initiatives for the production of green hydrogen is at the Dutch port of Eemshaven in the north of the country. This joint project by Shell and its partner Gasunie (Gas transport services) will use a large electrolyser powered by up to 10 GW of offshore wind power producing 800000 tonnes of green hydrogen by 2040.

In the UK ITM Power, which manufactures large electrolysers, is cooperating with Shell to produce a polymer electrolyte membrane electrolyser which will be capable of producing 1300 tonnes of renewable hydrogen per annum at Shell's refinery in Wesseling, Germany. This is still very

small compared with all the hydrogen that is consumed globally per annum which amounts to roughly 70 million tonnes. What is more about 95% of this hydrogen is produced by the steam reforming process which releases carbon dioxide to the atmosphere.

As the cost of renewable energy using offshore wind farms has reduced dramatically over the last decade this enables one to make projections as to cost of green hydrogen compared to traditional methods of hydrogen production. Assuming the cost of renewable energy continues to fall the route to producing green hydrogen at scale looks very promising. The European Commission strongly supports the eventual production of green hydrogen as well as clean hydrogen from natural gas followed by effective CCS systems fitted into the process.

Hydrogen as fuel for transport

In Germany the mechanical industry association (VDMA) advocates in its Power to X chain (P2X) the use of green hydrogen produced from electrolysers powered by excess wind farm electricity to manufacture in a series of subsequent processes ammonia and a range of fuels, such as methane, diesel, petrol, kerosene, ethylene and methanol. This will assist in improving the footprint of airlines that are heavy users of kerosene.

Could hydrogen be used to power cars? Hydrogen has to be combined with oxygen in a fuel cell to create electricity to drive the car's motors. Could this compete with a car powered directly from a battery? Not for the time being and also charging points for batteries are much more common unlike hydrogen filling stations. In UK one will not be able to purchase a petrol driven car beyond 2030 so one can see that beyond then many more hybrid cars will be on the market.

Strategies

What is evident is that green hydrogen is very much part of a number of Governments energy strategies as they seek solutions to meet the 2050 net zero goal. One hopes that China, one of the biggest polluters of greenhouse gases, will adopt similar strategies in their quest to meet a zero carbon initiative by 2060, their stated goal.

The UK has announced ten steps towards attaining a green industrial revolution. These are:

1. **Advancing offshore wind farms**
2. **Driving the growth of low carbon hydrogen**
3. New nuclear power stations
4. Accelerating the transition to Electric vehicles
5. Green public transport
6. Hydrogen fuel cell for small aircraft
7. Greener buildings
8. Investing in CCS
9. Protecting the natural environment
10. Boost green financing

The first two points, shown highlighted above, involve first accelerating the installation of wind farms and the production of blue hydrogen thus stepping up efforts to perfect the CCS process. One of its targets is to remove 10MT of CO₂ per annum at 2030. One hopes in the UK's long delayed energy strategy that green hydrogen will feature prominently using large scale electrolysers.

The European Commission also sees green hydrogen as a key element in its energy strategy. A report states, "that green hydrogen is a key priority to achieve the European Green Deal and Europe's clean energy transition." It is seen as a technology which can bridge the gap between electricity production from renewable energy and the goal of decarbonising a large share of the EU's energy consumption by 2050. In order to set the path for how hydrogen can be used in this way, and to make a first step towards setting the regulatory framework for a European hydrogen market, on 8 July 2020 the EU issued its "hydrogen strategy for a climate-neutral Europe" [1] (the EU Hydrogen Strategy). This report highlights that government support schemes are essential to enable green hydrogen to become cost effective.

I paraphrase the three phases stated in the hydrogen report:

Phase 1 (2020-24) Install 6 GW renewable hydrogen electrolysers to produce about 1 million tonnes of green hydrogen in the EU.

Phase 2 (2024-30) Install 40 GW of renewable hydrogen capable of producing 10 million tonnes of Green hydrogen

Phase 3 (2030-50) Renewable hydrogen technologies reach maturity.

Once again attaining the goals would require a huge increase in the manufacture of large electrolysers.

Finally, it is quite evident that a mix of Government subsidies and venture capital is needed on a massive scale if these goals are to be attained. However, the UK has supported during the past 15 months millions of workers through the furlough scheme where up to 80% of salaries was paid for workers not able to continue to work in their offices and once we are emerging from the pandemic such borrowed sums need to be repaid. Although current predictions are that the economy will recover quite rapidly it begs the question whether all the schemes discussed above will be supported as planned.

Were you aware that:

- The fashion industry produces about 2.1 billion tonnes of CO₂ p.a.

- 14% of global emissions come from animal products so eat less meat
- Driving an electric car reduces emissions by 1.9 tonnes p.a.
- Coffee machines, microwaves and speakers use energy on standby wasting 1.3 million tonnes of emissions p.a.
- Air drying instead of tumble drying reduces carbon by 90 kg p.a.
- UK households waste 4.5million tonnes of food p.a. and wasted food amounts to 8% of global carbon emissions

For further reading

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https://ec.europa.eu/energy/sites/ener/files/hydrogen_strategy.pdf

Report on IMPACIE 2020

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IMPACIE (Institute of Microwave Power Applications in Chemical Industry and Engineering) is an academic institute established together by researchers and industrial personages in the field of microwave technology and chemical engineering in China. It organizes national academic conferences biennially.

The second National Conference on Microwave Power Applications in Chemical Industries & Engineering (IMPACIE 2020) was held from 11th to 13th December 2020, in Zhanjiang, Guangdong, China. It received 131 submissions. About 200 attendees joined this conference and shared their latest research results and findings. More than 10 exhibitors including a gala dinner sponsor and a golden sponsor supported the conference. Besides Chinese participants, IMPACIE2020 also invited the JEMEA (Japan Institute of Electromagnetic Energy and Applications) president Dr. Hideoki Fukushima and vice president Prof. Yoshikawa to give plenary speeches on line.

The opening ceremony started at 8:30 a.m. of 12th December 2020. Eight plenary speeches were arranged next to the opening ceremony. Three sessions were held in parallel after the plenary session from 15:40 to 18:05 on 12th and the whole day of 13th December. The topics of those three sessions were: 1) Application of microwave in chemical industry, metallurgy, medicine, environmental treatment and food; 2) Microwave power devices and systems; 3) Microwave measurement and simulation.



Figure 1: Group photo of conference participants



Figure 2: IMPACIE president Prof. Kama Huang (left) and Prof. Cheng Zheng (right) during their plenary speech

Upcoming Events

Ampere 2021



CHALMERS



The planning for Ampere 2021 continues, but the change to online digital conference made the planning obsolete and had to be remade. On the other hand, all deadlines can be postponed since there are less preparations in advance. It is ever more important to stay updated by regularly checking the website www.ampere2021.org.

The authors of the accepted posters and presentations are welcome to write and upload a full paper of their research. The template for full paper preparation is also available on the website. The papers will be published in a digital book of proceedings issued by RISE, with a ISBN and DOI. All authors will also be encouraged to upload the paper on Zenodo, which will create an individual DOI for each paper and make the paper easily available with Open Access.

<https://zenodo.org/communities/ampere2021/>

XIX International UIE Congress

The Czech Committee of Electroheat and the University of West Bohemia will organize the XIX International UIE Congress on Electrotechnologies for Material Processing in Pilsen, 1. – 3. September 2021.

The Congress will include the following topics:

- Material processing by heating and melting
- Magnetohydrodynamics in industrial processes
- Production processes for innovative materials and products
- Process control and optimization
- Energy efficiency and sustainability of industrial thermal processes
- Efficient and sustainable energy management of buildings

Preceding the congress, a PhD course will be organized **from 27th August to 1st of September** for doctoral students and young researchers. The topic of the course will be “**Advanced numerical techniques for modelling and optimization of electrothermal processes**”. The course is intended for **12 students**. The cost of the course is **400 EUR** and includes also the student’s conference fee.

Conference website: <https://edison.fel.zcu.cz/html/ui2021/>

Job offers



Microwave Scientists and Engineers

SAIREM continues its development in the industrial applications of microwave and radiofrequency energy. To maintain that growth, we are looking to recruit several different profiles (scientists, technicians/engineers, sales/marketing) and offer our employees an interesting career in a company at the forefront of technology with a multicultural and international workforce, where the human dimension is a key strength and core value in our activity.

If you are interested in joining us, please send your application to bschneyder@sairem.com. It will be studied with great attention.



Sales Manger

To support our growth, we are seeking to hire a high-performing Sales Manager for North- and South-America. You will be responsible for providing State-of-the-Art Microwave Technology to emerging markets like Lab Grown Diamonds, New Materials and sustainable Green Power.

To keep our company competitive and innovative, you will be in charge of managing sales by developing business plans, meeting forecasted sales, recruiting new customers and coordinating with Muegge GmbH in Germany on new products and developments. You also will be tasked to oversee sales activities by tracking targets and providing necessary support to our customers and internally to your team.

Please send your application to Esperanza.Lofstrand@muegge-gerling.com

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- Technology-transfer and commercialization.
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- Technological and market forecasts.
- Comments, views, and visions.
- Interviews with leading innovators and experts.
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- Economical and practical considerations.
- Upcoming events, new books and papers.

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We believe that this seemingly less-rigorous editorial approach is essential in order to accelerate the circulation of ideas, discoveries, and contemporary studies among the AMPERE community worldwide. It may hopefully enrich our common knowledge and hence exciting new ideas, findings and developments.

Please send your submission (or any question, comment or suggestion in this regard) to the Editor in the e-mail address below.

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