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# Laser Processing of Materials for the Energy Transition

## Applications to Fuel Cell Technologies

By

**Tommaso Serra**

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**Supervisors:**
Prof. Candido Fabrizio Pirri, Supervisor
Prof. Marzia Quaglio, Co-Supervisor
Prof. Giancarlo Cicero, Co-Supervisor

**Doctoral Examination Committee:**
Dr. Marco Etzi Coller Pascuzzi, Referee, Istituto Italiano di Tecnologia
Dr. Fabiola Liscio, Referee, Consiglio Nazionale delle Ricerche (CNR-ISMN)
Dr. Angelica Chiodoni, Istituto Italiano di Tecnologia
Dr. Alberto Ballesio, Consiglio Nazionale delle Ricerche (CNR-IMEM)
Prof. Stefano Bianco, Politecnico di Torino
Prof. Carlotta Francia, Politecnico di Torino

Politecnico di Torino
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Tommaso Serra
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# Declaration

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# Laser Processing of Materials for the Energy Transition

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This PhD thesis discusses and demonstrates the advantages and novelties introduced by laser-assisted processing techniques in the production chain of fuel cells for the hydrogen economy. Hydrogen and fuel cells have been recognized as integral in the vision of a carbon-neutral energy economy. However, the low availability of both their related infrastructures and consumer products currently hinders their diffusion. Tailored laser-assisted processes could offer significant improvements in manufacturing fuel cell electrodes and catalyst layers, which are crucial components in determining a fuel cell fabrication and assembly cost. The overall fuel cell production chain could be made simpler, less time- and energy-consuming and more more streamlined with the introduction of laser-assisted processes in certain key steps of production related to electrodes and catalyst layers. This could be achieved by taking advantage of the unique properties of laser-assisted processes that are not found in other established approaches. The number of steps and time necessary to obtain the final fuel cell product could be immensely reduced with novel but unconventional laser-assisted processes. Moreover, laser-assisted processing is transversal to a wide range of materials. Therefore, it was possible to make use of materials other than the extremely critical Platinum-Group Metals catalysts. All together, these properties render laser-assisted processes a powerful tool in the effort of making fuel cells more widely and easily accessible. The data to support these claims was collected by constantly comparing the obtained materials and processes against the state-of-the-art standard for fuel cells in application-relevant operative conditions. The main results presented in this thesis are three. They are independent but complementary to each other in offering alternative solutions to conventional fuel cell fabrication methods. The first solution is an innovative process for the fabrication of a porous electrode entirely based on Laser-Induced Graphene. This process allowed the easily scalable production of ready-to-use patterned fuel cell electrodes by photothermal conversion of Kapton® films into graphene-like material under $CO_2$ laser irradiation in ambient atmosphere. The novel approach based on a laser exposure on each side of the Kapton® allowed the realization of all-LIG electrodes, rather than conventional planar electrodes

supported by the remaining polymer, enabling LIG to be employed in fuel cells, where through-plane electrical conductivity and porosity are mandatory. This achievement allowed the deposition of a national and international patent protecting this process. The second solution is the successful fabrication of an electro-catalytically active electrode based on Laser-Induced Graphene. The catalytic properties of this electrode were guaranteed by fine tuning the polymeric precursors' composition and morphology to achieve a desirable in-situ doping of the Laser-Induced Graphene during the photothermal conversion of the polymeric precursors under $CO_2$ laser radiation. This electrode underwent tests to confirm its capability to correctly perform the cathodic Oxygen Reduction Reaction occurring in fuel cells and proved to be competitive with platinum-based catalysts in acidic pH environments. The final solution involves the synthesis of a manganese oxide catalyst layer for the alkaline Oxygen Reduction Reaction via localized $CO_2$ laser-induced thermal annealing of manganese acetate nanofibers in ambient conditions. By comparing equivalent loadings of laser-treated and conventional furnace-treated manganese oxide catalysts between each other, it was possible to identify the clear advantages provided by the laser-assisted solution. The localized laser-induced thermal annealing was able to better preserve the morphology and nano-scale features of the nanofibers, producing a catalyst featuring higher active surface area and accessible catalytic sites for reactions, which are highly desirable features to improve the effectiveness of electro-catalysts. Overall, this resulted in lower Oxygen Reduction Reaction overpotentials and considerably higher achievable current densities in favor of the laser-induced manganese oxide. To conclude, the studies performed in this thesis aim at demonstrating the effectiveness of laser-assisted processing in the continued effort towards making the hydrogen-based economy more viable. A hydrogen fuel cell production chain incorporating laser-assisted processing for the fabrication of its components would be less energy-demanding and more streamlined. At the same time, the unique properties of laser-assisted processing that differentiate it from established processes also guarantee that unconventional solutions based on unusual materials are possible while maintaining competitive performance with commonly established approaches.