4.7 Energy harvesting and energy converter devices

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Current state of the field

Thermal spray has been contributing in developing energy applications, which fit well into present-day scenario of energy conservation and promise potential for large market penetration. This offers, on one hand, an unprecedented opportunity for mass production of innovative components in emerging markets by means of advanced thermal spray technology. On the other hand, this presents challenges of improving the existing and developing new spraying devices and methods, feedstock materials, and diagnostic and control tools to have coatings with better engineered structures and characteristics. Of these applications, some of the key devices include:

- Thermo-Electric Generators,
- Alkaline Water Electrolysers,
- Polymer Electrolyte Membrane Water Electrolyser,
- High Temperature Solid Oxide Cells, either in fuel cell mode for power generation or as electrolysers for steam electrolysis or co-electrolysis of steam and CO_2,

At present, most of these devices are typically produced by wet powder/powder metallurgy processing that includes sintering steps needing high temperatures and long process time. This limits the spectrum of usable materials, as sintering can be critical for materials that can exhibit undesired modifications in their composition and structure due to diffusion or for instance decomposition. In addition, these processes have limitations concerning geometry, size of the products, and substrate materials. In contrast, thermal spraying has the unique ability that at the completion of the fast spray procedure, the product is in the desired final state and in most cases no or nearly no further processing is needed. As sintering can be avoided, the danger of material inter-diffusion or other negative alterations can be reduced. Furthermore, thermal spraying allows, in principle, for a near-net shape production of multi-layered structures with constant or controlled functionally graded composition of material and porosity with relatively low constraints concerning size and geometry (Ref 1).

Thermo-Electric Generators (**TEG**)

Thermoelectric generators are solid state devices that convert heat directly into electricity. A TEG consists of two legs of dissimilar thermoelectrically semi-conducting materials, one n-type and other p-type, which take advantage of the so-called Peltier-effect of materials with high Seebeck-coefficient, having high electrical and low thermal conductivity, and results in electrical voltage if a temperature gradient is applied across these semiconductors (Ref 2,3).

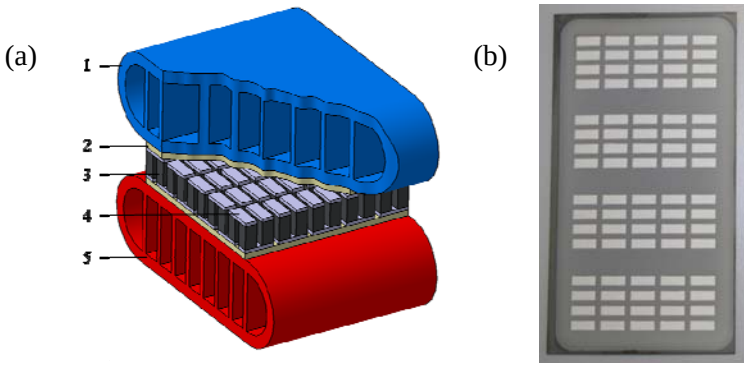


Fig 39: (a) Schematic of a thermoelectric generator (TEG). 1) Cold side heat exchanger, 2) Insulation, 3) Thermoelectric semiconducting materials, 4) Electrical connections, 5) Warm side heat exchanger

(b) Plasma sprayed half-TEG module

They can be applied for example to generate electricity in power plants or in cars to use the waste heat. Different thermoelectric materials are developed in the temperature range up to 1000 °C with each of them exhibiting optimum properties at specific temperature. In order to use a broader temperature range and to increase the output voltage and the efficiency, development is under way to connect in series several elements suitable for different temperature ranges, starting with a high temperature element. Some of the typical materials are intermetallic compounds like iron-silicides or cobalt-antimonites (Ref 4,5). For this application thermal spray exhibits the fundamental advantage that the multilayers can be made consecutively. This holds under the precondition that suited feedstock

material is available. Hence, multi-layered TEGs represent an interesting challenge for thermal technology and a wide potential for development (Ref 6,7).

Alkaline Water Electrolysers (AWE)

Alkaline water electrolysers have been around since many years for the production of hydrogen. However, still today, hydrogen is primarily produced by reforming of natural gas or hydrocarbons due to lower cost. Increased awareness that the fossil resources are limited and we need to reduce our emission footprint, led to re-emergence of interest for hydrogen by electrolysis. Coupling AWEs with renewable energy sources such as solar or wind energy and to use produced hydrogen as energy storage media, especially when a surplus of power exists, has seen recent growth.

AWEs have conventionally two metallic electrodes, where on the cathode side hydrogen and at the anode oxygen are produced in an electrolyte of an aqueous solution of for example KOH. To attain high production yield and lower costs of AWEs, the conventional electrodes of AWEs should be replaced by improved ones, with better alloys exhibiting large activated surfaces leading to high efficiency and ability for intermittent operation, which is inherent with renewable energy sources (Ref 8). Electrodes of technical AWEs can have a size surmounting a square meter; therefore sintering techniques are hardly applicable.

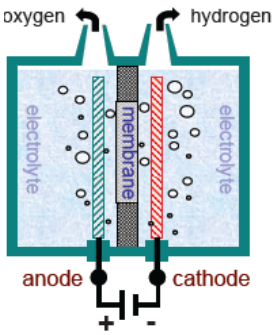
The AWE electrodes of DLR consist of metal sheet substrates coated with plasma sprayed active electrode layers. For the cathode surface NiAlMo-alloy powder is sprayed and for the anode NiAl-Co_3O_4 (Ref 9). For activating of the electrode surfaces most of the Al-content is leached resulting in a highly structured Raney-MoNi-matrix with high specific surface area, and therefore lowered polarisation losses (higher efficiency). In the frame of different projects, namely HYSOLAR, DLR's developed vacuum plasma sprayed (VPS) electrodes were tested as laboratory-sized electrodes leading to an efficiency of over 80% of the test electrolysers (percentage of electrical energy converted into the chemical energy of the produced hydrogen), and the suitability for intermittent operation could be demonstrated. Also large electrodes proved positively in technical electrolysers (Ref 10).

Several challenges, however, remain to be addressed, which include beneath others:

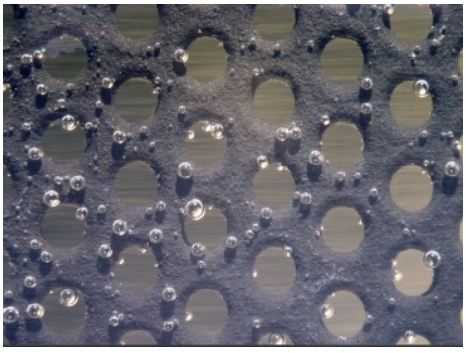
- Optimisation of the spray material and the well bonded electrode layer structure.
- Investigation of degradation mechanisms.
- Industrialisation of production of large sized electrodes, suited for renewable energy sources.

Fig 40: (a) Schematic of alkaline water electrolyser(AWE)

(b) Plasma sprayed hydrogen side AWE electrode under operation with formation of H_2 bubbles.



(a)

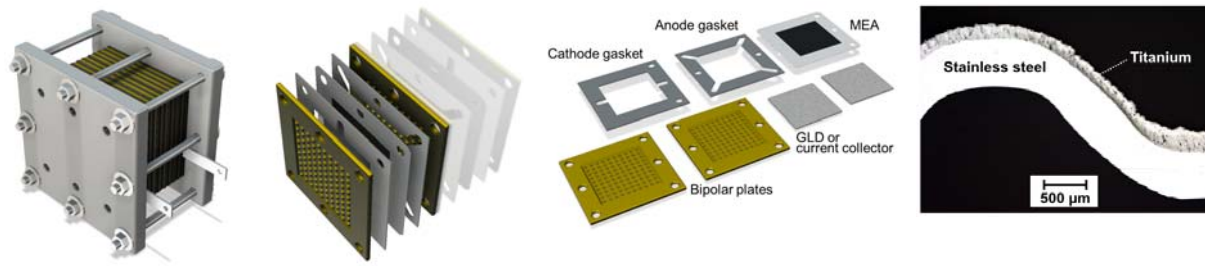


(b)

Polymer Electrolyte Membrane Water Electrolyser (PEM-WE)

Polymer electrolyte membrane water electrolysis (PEM-WE) has emerged as one of the most promising technologies for large scale and efficient hydrogen production from surplus power. It offers distinct advantages over AWEs including ecological cleanness due to use of only deionized water instead of aqueous solutions, smaller footprint and mass, lower gas crossover and higher purity of produced hydrogen gas, and expected reduced operating costs (Ref 11). Thermal spraying has limited applicability to the electrochemical active components of PEM-WEs, i.e. membrane-electrode-assembly (MEA), but has been showing promising results for the components Gas Diffusion Layer (GDL) and Bi-Polar Plates (BPP). Due to highly corrosive environment in PEM-WEs, both GDL and BPP are made of Titanium. The use of Ti material, and its machining makes the costs of these components very high as suggested in recent EU studies (Ref 12) that GCL and BPP correspond to around 2/3 of total costs of PEM-WEs (noble metal catalysts attribute to less than 10 %). The cost of GDL and BPP is further enhanced by the fact that additional coating on top of Ti is needed as Ti

exhibit passivation during operation leading to high resistance. In recent work, DLR has published promising results of their patented approach in which stainless steel BPP are used protected by dense coatings of Ti / Au and Ti / Pt produced by thermal spraying or combination of thermal spraying and PVD (Ref 13). Similarly, stainless steel meshes based GDL were introduced with thermally sprayed highly porous Ti coating along with secondary materials to limit passivation. These promising results open possibility to further address the pending challenges including feedstock powder development, optimizing spray method for either fully dense or controlled porous layers, and large scale production, etc.



(a) (b) (c) (d)

Fig 41: Polymer membrane water electrolyser (PEM-WE). a) stack, b) single repeat unit cell (c) components of a cell, and d) cross sectional micrograph of coated bipolar plate

High Temperature Solid Oxide Cells

Solid Oxide Fuel Cell (SOFC)

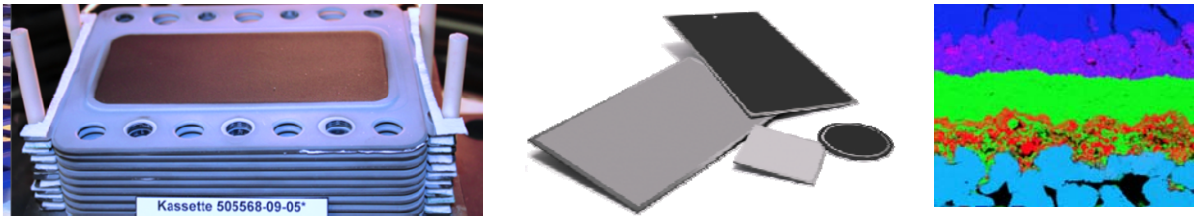
High temperature solid oxide fuel cells (SOFC) are not subjected to the "Carnot Limitation" and convert directly chemical energy into electricity with high efficiencies reaching 60% in stand-alone operation and above 80% if waste heat can be used. SOFC have reforming properties and can be fuelled by hydrocarbons. Due to these characteristics, SOFCs are gaining interest for stationary applications for combined heat and power supply, and as electricity source in automotive as on-board power generators called "Auxiliary Power Units" (APU). Operating typically between 650 and 800 °C, SOFCs consist of three main components, the cathode, (i) the air electrode, where air-oxygen is reduced to negatively charged oxygen-ions (O^{2-}), (ii) the dense electrolyte, which should only be "permeable" for such ions, and (iii) the anode, the fuel electrode, where these ions react with the fuel (H_2 or/and CO) releasing electrons, which return to the cathode side via an external load, generating thereby a usable voltage/electrical power. Further products at the anode side are steam and CO_2. The generated voltage value of such a cell in operation is typically around 0.7V; therefore, several cells have to be arranged in series (stacked) to get a usable voltage and power, where so-called metal interconnectors establish the electrical contact between adjacent cells.

Thermal spraying has been used to produce all the electrochemical active components which are composed of (i) perovskites for the cathodes, (ii) yttria stabilized zirconia for the electrolytes, and (iii) a mixture (cermet) of yttria stabilized zirconia and nickel for the anodes (Ref 14). Producing electrodes using thermal spraying good control of the microstructure is required to have high conductivity, high active surface area, and excellent permeability for flow of gases. Conventional thermal spraying with agglomerated feedstock and suspension plasma spraying have shown potential towards achieving those characteristics but further development is needed. Probably the biggest challenge lies with the electrolyte, which should exhibit a low resistivity for the oxygen-ion diffusion and impermeability for electrons and gases (in particular hydrogen). This can be achieved either by having a suitable material or making the electrolyte as thin as possible (in sintered cells it is typically below 10 µm). These two demands of low thickness and high gas tightness, pose the main challenge for the production of cells by thermal spraying. Until now, "very high velocity plasma spraying", HVOF, suspension plasma or suspension HVOF spraying have been unable to offer a quality matching to that by sintering. Improved processes and new ones like "Suspension and Solution Plasma Spraying" allowing for the use of very fine powders or even to produce the layers in a plasma chemical way, both could open, hopefully, a potential for thin electrolytes of required density or of other high quality cell components (Ref 15,16). Besides these active components technical cells have also further components which can be produced by thermal spraying including Cr- protection layer on interconnects, solderable insulating layers for sealing of interconnect plates between adjacent cells in a

stacks, diffusion barrier layers to prevent inter-diffusion between the components. Several groups including DLR have shown feasibility to produce all or some of these components by thermal spraying; quality and performance need improvement to be competitive to other production technologies (Ref 17,18).

Solid Oxide Electrolysis Cell (SOEC)

About 30 years ago the German company Dornier was around with their project named “Hot-Elly” to produce hydrogen with high temperature electrolysis. The electrolysers consisted of tubes of series connected small cell rings. The idea of this approach was to reduce the required electricity demand for electrolysis by feeding directly high temperature steam, because this energy form is not burdened by efficiency constraints as it is with the electrical share. This project was abandoned already about 20 years ago, but the gained technological knowledge was helpful and important for following work on SOFCs, because the SOFC-process represents the inversion of the SOEC-process, therefore, materials and material processing are almost similar, with exception that the requirements and operating conditions are even harder with SOECs compared to SOFCs. The new thinking about energy supply and the need for better and more efficient use of energy was the reason why activities on SOECs were started again, basing to large extent on recent experience with SOFCs and their production (Ref 19). Therefore, concerning thermal spray almost all is valid, here, which was discussed above with SOFCs.



(a) (b) (c)

Fig 42: Solid oxide cell a) stack, b) plasma sprayed cell (d) cross sectional micrograph of coated cell: (bottom to top) substrate, fuel electrode, electrolyte, oxygen electrode, current collector

References

1. R. Henne, Solid oxide fuel cells: A Challenge for Plasma Deposition Processes, J. Therm. Spray Technol., 2007, 16(3), p 381-403
2. F. D. Rosi, Thermoelectricity and Thermoelectric Power Generation, Solid-State Electronics, 1968, 11, p 833-868
3. Byung Deok In et al.: The Study of a Thermoelectric Generator with Various Thermal Conditions of Exhaust Gas from a Diesel Engine, Int. J Heat and Mass Transfer, 2015, 86, p 667-680
4. Kwan-Ho Park et. al.: Thermoelectric Properties of Skutterudite $In_yCo_{4-x}Fe_xSb12$, J. Korean Physical Society, 2012, 60(10), p 1485-1490
5. L. Zhang et al.: Mechanical Properties of Filled Antimonide Skutterudites, J. Mat. Sci. & Engin.: B, 2010, 170(1-3), p 26-31
6. J. Schilz, M. Riffel, R. Mathesius, G. Schiller, R. Henne, R.W. Smith, Plasma Spray Forming as a Novel Production Method for Thermoelectric Materials, Proc. XV International Conference on Thermoelectrics (ICT 96), March 26-29, 1996, Pasadena, CA, USA
7. T.O. Freitag et al.: Plasmaschichtentwicklung eines stoffschlüssigen thermoelektrischen Moduls, 2013, 69, p 155-166
8. H. Wendt, Processes for Water Splitting, in “Hydrogen as Energy Carrier”, C.-J. Winter, J. Nitsch, Eds., Springer Berlin, Heidelberg, 1986, p 174-185
9. G. Schiller, R. Henne, and V. Borck, Vacuum Plasma Spraying of High-Performance Electrodes for Alkaline Water Electrolysis, J. Therm. Spray Technol., 1995, 4(2), p 185-194
10. G. Schiller, R. Henne, P. Mohr, and V. Peinecke, High Performance Electrodes for an Advanced Intermittently Operated 10-kW Alkaline Water Electrolyzer, 1998, 23(9), p 761-765
11. P. Millet, N. Mbemba, S. Grigoriev, V. Fateev, A. Aukauloo, C. Etiévant, Electrochemical Performances of PEM Water Electrolysis Cells and Perspectives, Int. J. Hydrogen Energy 2011, 36, p 4134–4142.

12. L. Bertuccioli, A. Chan, D. Hart, F. Lehner, B. Madden, E. Standen, Study on Development of Water Electrolysis in the EU-Final Report. E4tech Fuel Cells & Hydrogen Joint Undertaking; 2014
13. S. Gago, A. S. Ansar, P. Gazdzicki, N. Wagner, J. Arnold, K. A. Friedrich, Low Cost Bipolar Plates for Large Scale PEM Electrolyzers, in ECS Transactions 64, October 2014
14. D. Soysal, J. Arnold, P. Szabo, R. Henne, S.A. Ansar, Thermal Plasma Spraying Applied on Solid Oxide Fuel Cells, J. Therm. Spray Technol., 2013, 22(5), p 588-598
15. L. Jia, C. Dossou-Yovo, C. Gahlert, F. Gitzhofer, Induction Plasma Spraying of Samarium Doped Ceria as Electrolyte for Solid Oxide Fuel Cells, Thermal Spray 2004: Advances in Technology and Application, ASM International, May 10-12, 2004 (Osaka, Japan), 2004, p 85-89
16. Y. Shen, V.A.B. Almeida, F. Gitzhofer, Preparation of Nanocomposite GDC/LSCF Cathode Material for IT-SOFC by Induction Plasma Spraying, J. Therm. Spray Technol., 2011, 20(1-2), p 145-153
17. T. Franco, R. Ruckdäschel, M. Lang, G. Schiller, P. Szabo, Diffusion and Protecting Barrier Layers in a Substrate-Supported SOFC Concept, Proceedings 7th European Solid Oxide Fuel Cell Forum, Lucerne, Switzerland, 3-7 July 2006, PO802
18. J. Arnold, S.A. Ansar, U. Maier, R. Henne, Insulating and Sealing of SOFC Devices by Plasma Sprayed Ceramic Layers, Thermal Spray 2008: Crossing Borders, on CD-ROM, E. Lugscheider, Ed., June 2-4, 2008, Maastricht, The Netherlands, DVS-German Welding Society, 2008
19. G. Schiller, A. Ansar, M. Lang, O. Patz, High Temperature Water Electrolysis Using Metal Supported Solid Oxide Electrolyzer Cells (SOEC), J. Appl. Electrochem., 2009, 39, p 293-301