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Achieving Cost Reduction in PEM Electrolysis by Material Development

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Abstract

Hydrogen is expected to play an important role as a crosslinking technology between power generation on one hand and transport and industry on the other hand. It can directly replace fossil fuels in transport and industry when produced by water electrolysis renewable energies such as solar or wind, which are converted with low efficiencies. The relevant technologies are either the mature alkaline electrolysis or the newer proton exchange membrane (PEM) water electrolysis. For PEM electrolysis in particular, key components that determine the stack cost are the titanium-based contact elements, such as the bipolar plates (BPP) and the current collectors (CC), and the high iridium loading of electrocatalyst for the OER in state of art membrane electrode assemblies (MEA). However, the cost structure depends on the specific design of the electrolyser. This paper will discuss strategies for cost reduction by synthesizing unsupported and supported IrO_x and IrRuO_x electrocatalyst with the aim of lowering the high loading. Our synthesis procedure consists of producing nano-sized iridium particles by reducing iridium chloride (IrCl₃) with conventional sodium borohydride at room temperature and in water-free environment. This concept can also be applied to supported and alloy electrocatalysts. The supports need to be highly stable and exhibit sufficient electronic conductivity. The enhancement of activity achieved with improved electrocatalyst reaches a factor of about 15 with respect to the best commercially available electrocatalyst. Additionally, the cost reduction achieved by a titanium coating for stainless steel BPPs or CCs for PEM electrolysis will be discussed. We use vacuum plasma spraying (VPS) to coat either dense coatings for corrosion protection of stainless steel components or build up titanium diffusion layers with defined porosity as contact elements for the MEA. The conductivity of the titanium coating can be improved by well-known Pt or Au additions; however, we have also developed promising non-noble conductivity enhancement elements. Furthermore, the VPS coating and production procedure is adaptable to large-scale industrial production.

Introduction

Proton exchange membrane (PEM) water electrolysis is considered as one of the most promising technologies for hydrogen production from renewable energies, which has a potential to penetrate the market in near future and enable the Power-to-Gas (P2G) application on a wider scale (Fig. 1). However, reducing capital cost of PEM electrolyzers without losing efficiency is one of its most pressing challenges. Detailed cost analysis has shown that under future scenarios with high share of renewables, limited operation of 2000-3000 h per annum electricity (OPEX) and investment cost (CAPEX) are of equal importance for P2G plants [1]. A recent study funded by FCH-JU demonstrates that the CAPEX of PEMEL stacks – which however depends on the specific stack design – are dominated by the cost of bipolar plates [2]. In addition also current collectors contribute also significantly to the cost of the stack whereas the catalysts are presently of minor importance. Nevertheless, there is a wide perception that the anode catalysts may be the real hindrance for this technology. One reason is the sluggish oxygen evolution reaction (OER) kinetics on most electrocatalysts and their insufficient durability due to the highly corrosive working environment [3]. To date, Ir-based catalyst is still the only feasible option to promote OER in the anode of a PEM electrolyzer due to its high activity and considerable stability. Still, the most often used catalyst is rutile IrO₂, which is stable but not very active. Not only the high cost of the precious metal, but also the scarcity of Ir in the earth crust are barriers on the road to commercialization of PEM electrolyzers. Therefore, highly active and stable OER catalysts in acid electrolyte with ultra-low Ir loading are required to address this issue.



Fig. 1. 1.5 MW PEM electrolyzer for P2G application at Reitbrook, Hamburg Germany (courtesy of Uniper and partners [4]).

2. Highly active Ir-based anode catalysts

Generally, there are two approaches to improve an electrocatalyst activity: i) increasing the intrinsic activity of each active site; ii) increasing the number of active sites on a given electrode. Interestingly, a screening study of different technical membrane electrode assemblies in a rainbow stack revealed that Ir-black exhibited a much higher activity compared to common rutile Ir oxides, while it is still sufficiently stable for the PEM electrolysis application [5]. As a consequence, Ir-black with IrO_x surface and metallic core is our benchmark catalyst. Under this frame, amorphous IrO_x nanoparticles (Ir-nano) are prepared to achieve a high intrinsic activity, displaying five-fold higher OER activity than

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commercial Ir-black [6]. The structure and OER activity of this nanoscale iridium catalyst, in comparison to Ir-black, are shown in In Fig. 2 and Fig.3, respectively.

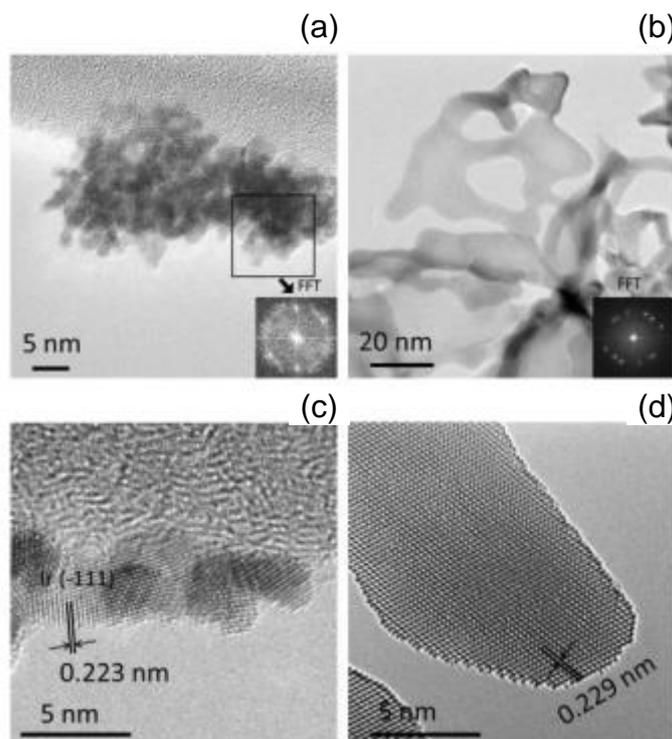


Fig. 2. Transmission electron microscopy (TEM) of (a) Ir-nano and (b) Ir-black. The corresponding high resolution micrographs are shown in (c) and (d), respectively [6].

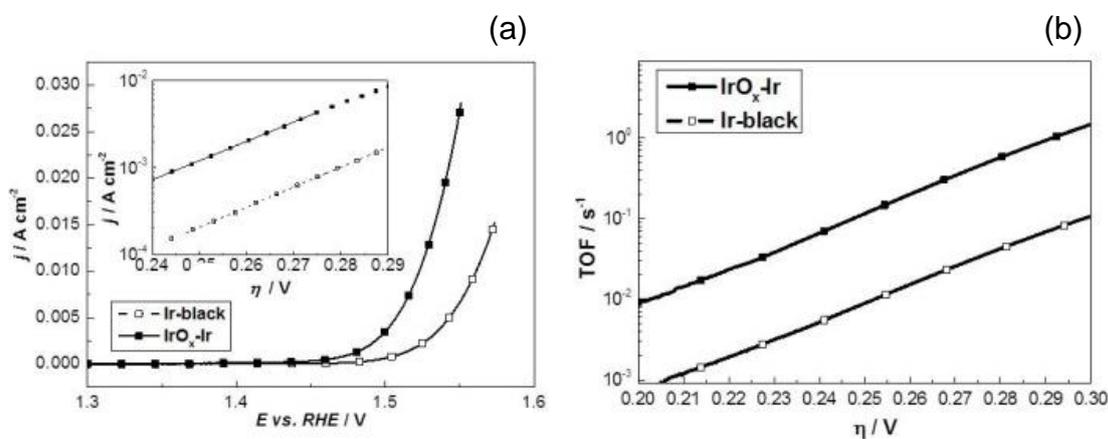


Fig. 3. (a) Current-potential and (b) turnover frequencies of Ir-nano and Ir-black. Sweep rates of 5 mV s⁻¹ in Ar-saturated 0.5 M H₂SO₄ electrolyte.

In addition, a highly active Ir electrocatalyst derived from amorphous IrRuO_x via an electrochemical way was developed, demonstrating 13 times higher OER activity compared to the rutile phase of IrRuO₂ [7], Fig. 4. The stability was evaluated by PEM electrolyzer measurements, showing no cell potential decrease during ca. 400 h test.

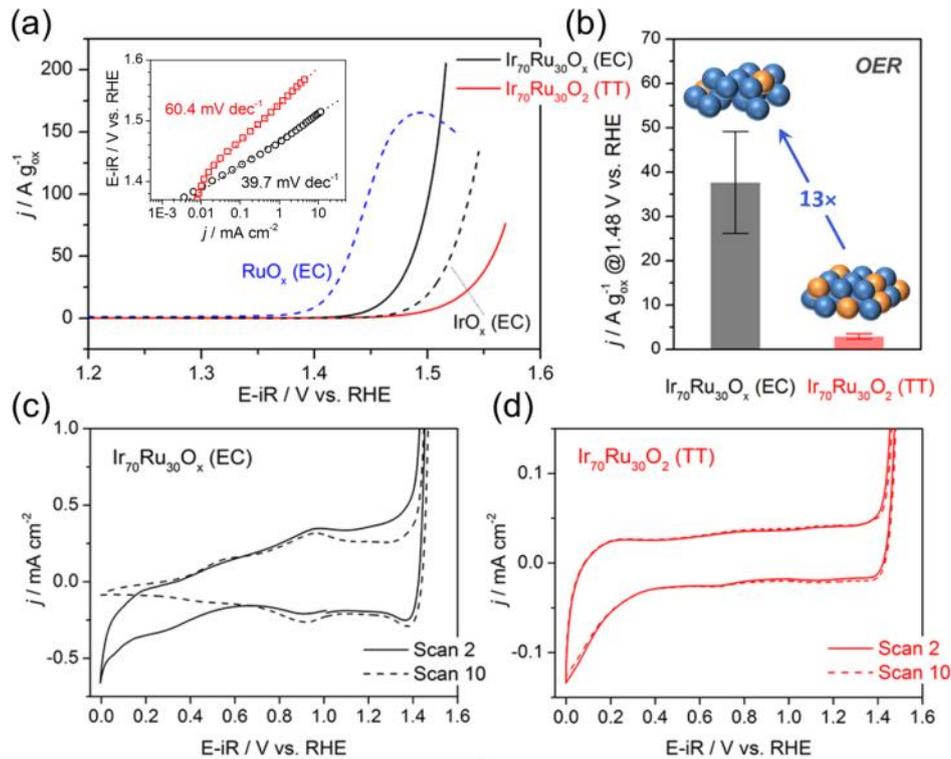


Fig. 4. (a) Current-potential, (b) mass activity @ 1.48 V vs. RHE. Cyclic voltammetry of (c) amorphous IrRuO_x and (d) rutile IrRuO₂. Sweep rates of 5 mV s⁻¹ in N₂-saturated 0.05 M H₂SO₄ electrolyte [7].

Regarding the second approach, we use electro-conductive ceramics as supporting materials to increase the active sites number, thus achieve an improved Ir utilization. First, IrO_x was deposited on Magnéli phase Ti₄O₇ showing higher OER activity, in terms of Ir mass, compared to Ir-black [8]. Further on, SnO₂:Sb aerogel (developed by Armines, France) was introduced as a support [9]. By taking advantage of the highly porous structure of the aerogel support, Ir/SnO₂:Sb-aerogel allows a decrease of more than 70 wt.% precious metal usage in the catalytic layer, while keeping the same activity and significantly enhancing the stability compared to its unsupported counterpart, Fig. 5.

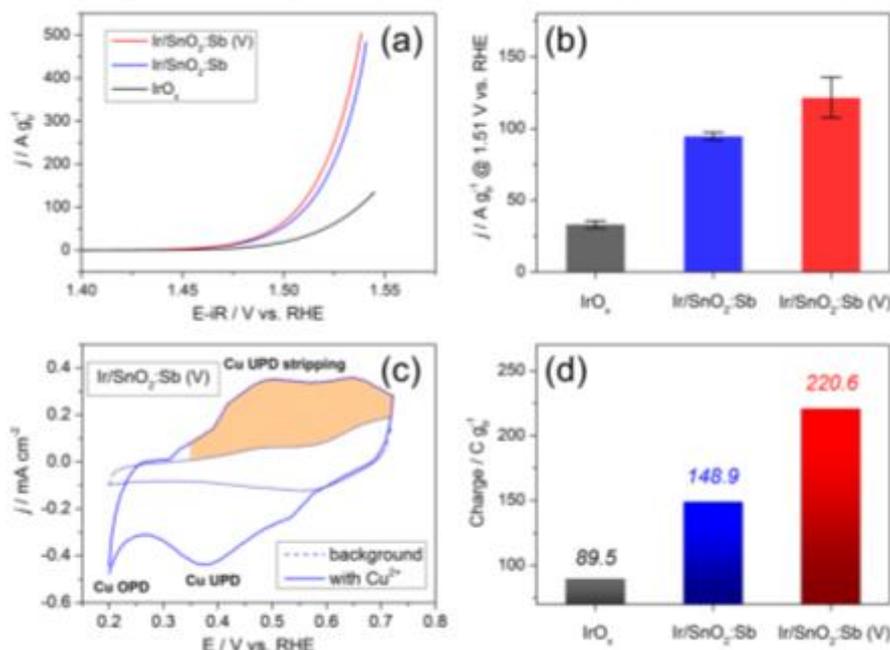


Fig. 5 (a) OER activity performance of Ir/SnO₂:Sb (V), Ir/SnO₂:Sb and unsupported IrO_x, 25 °C, N₂-saturated 0.05 M H₂SO₄, 5 mV s⁻¹, 1600 rpm; (b) mass activity comparison under an overpotential of 280 mV; (c) Cu under potential deposition (UPD) profile of Ir/SnO₂:Sb (V); (d) charge comparison based on Cu-UPD stripping peaks among three catalysts [9].

Lastly, advanced in operando techniques, in particular near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS), are applied to provide insight into the potential-dependent specific chemical state of the catalysts surface and explore their electrocatalysis and stabilization mechanisms [10]. RuO₂ and IrRuO₂ were investigated under water splitting condition in the form of the Aquivion-based membrane electrode assemblies (MEA). We found that Ir protects Ru from the formation unstable hydrous Ru^{IV} oxide and OER occurs through a surface Ru^{VIII} intermediate.

The high amount of required noble metals, such as Ir and Pt, are often mentioned as the bottleneck for its commercialization of PEM electrolyzers and indeed, the catalysts could limit its availability at the gigawatt scale [11]. The reduction of precious metal content by improving the activity of the electrocatalytic properties is a main priority in PEM electrolysis research and it has been in the focus of our efforts as well as other groups.

3. Coatings for bipolar plates and current collectors

The catalysts have currently a relatively small influence on the capital cost. The main part of the stack costs accounts to the interconnectors consisting of bipolar plates (BPP) and current collectors (CC), also called gas diffusion layers (GDL). These components account together for 50 to 70 % of the stack cost depending on the design [1,2]. Their high cost is due to the fact that the employed materials need to withstand corrosion at high anodic potentials in acidic environment. Currently, only Ti is the material of choice for the anode side. However, a semi-conductive oxide layer grows on its surface over time. In this context, a lucrative solution is to replace the Ti BPPs by coated stainless steel. Vacuum plasma spraying (VPS) technology can be used to produce highly dense Ti coatings to protect stainless steel BPPs from the oxidative conditions in the anode side [12]. Surface modifications with Au [13] or Pt [14] improve the conductivity of the Ti coating, but also Nb coatings can extend the long-term stability of the electrolyzer [15].

A rainbow stack was assembled to investigate the impact of surface material on anode and cathode side. The coatings were tested and compared against commercially coated-titanium BPPs. The cells were separated in two categories: category 1 corresponds to cells with precious metal surface modification and category 2 to cells with valve metals (Ti or Nb) on the surface on the cathode side, see Table 1.

Table 1. Rainbow stack configuration: Stainless steel BPPs (92E Stack, Hydrogenics) with the corrosion resistant Ti coating: Ti/ss. BPPs with additional surface modification of Pt and Nb, Pt/Ti/ss and Nb/Ti/ss, respectively. E300 and E400 MEAs (Greenerity) were used [15,16].

Cell	BPP Anode	BPP Cathode	Category
1	Commercially coated Ti	Commercially coated Ti	1
2	Commercially coated Ti	Commercially coated Ti	1
3	Ti/ss	Commercially coated Ti	1
4	Ti/ss	Ti/ss	2
5	Pt/Ti/ss	Ti/ss	2
6	Pt/Ti/ss	Pt/Ti/ss	1
7	Nb/Ti/ss	Pt/Ti/ss	1
8	Nb/Ti/ss	Nb/Ti/ss	2

The stainless steel BPPs were coated on both sides with Ti to avoid any possible galvanic corrosion of the cathode surface when in contact with the MEA during standby periods. However, Ti in contrast to stainless steel, is susceptible to hydrogen embrittlement. Therefore a protective coating or surface treatment on the cathode side for the massive titanium BPPs, as well as for Ti-coated stainless steel ones is required. This assumption is supported with the results presented in Fig. 6, which correspond to a long-term performance of the stack. The lower the cell potential (E_{cell}) corresponds the higher the efficiency of the PEM electrolyzers. Cell 4, 5 and 8, which have wither Ti or Nb/Ti coatings on the cathode side, show from the very beginning of the test, significantly worse performance compared with those having Pt. The high E_{cell} can be explained by hydrogen embrittlement of the valve metals.

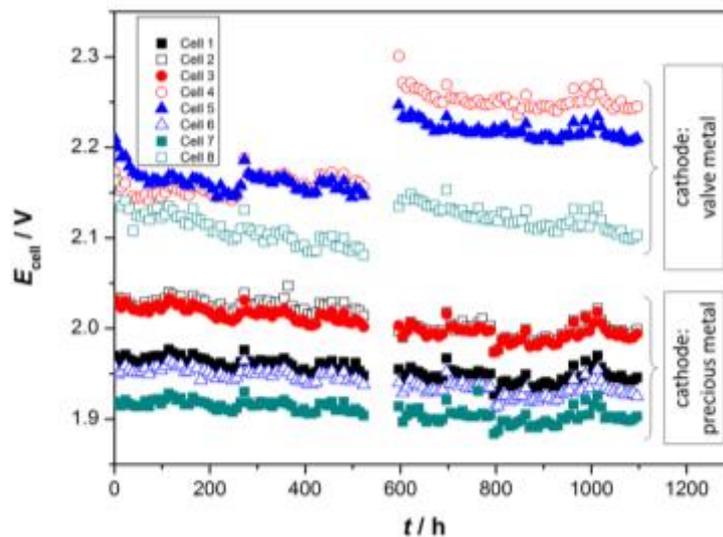


Fig. 6. Durability test for 1000 h at constant current density of 1 A cm^{-2} . Coatings of Cell 1-8 are enlisted in Table 1.

After 500 h the electrolyzer was switched off for several hours and oxygen was able to diffuse to the cathode side, passivating even further the material. The consequence is a rapid potential increase in the next 500 h of the test. The commercial cells and those coated with Pt on the cathode side show in general a much higher performance. Here it is also possible to distinguish the positive impact of the Pt and Nb surface modification for the anode side. Cell 3 has higher performance as cell 6 and 7, which have surface modifications. Those cells show also a stable behavior during the entire testing protocol.

The post mortem analysis of the BPPs proves the protective behavior of the thick film coating of Ti even after 1000 h test in real PEM electrolysis conditions. Scanning electron microscopy (SEM) images of the BPPs show in every case the protective effect of the Ti coating. Differences can be observed for the thin film surface modification. For the anode side Pt and Nb are still well adhered to the titanium coating (Fig. 7b and 7d), but for the cathode side only Pt is still in contact to Ti. Fig. 7c shows clearly that the Nb thin film coating is delaminated.

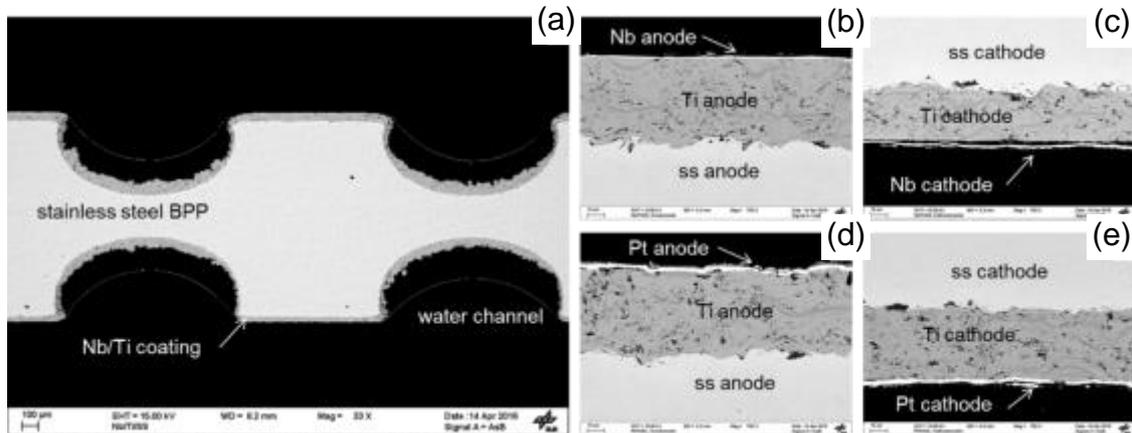


Fig. 7. Post mortem SEM analysis after 1000 h in use as electrolyzer BPP. (a) Overview, (b) Nb/Ti/ss anode, (c) Nb/Ti/ss cathode, (d) Pt/Ti/ss anode, (e) Pt/Ti/ss cathode, (d) Ti/ss anode, (e) Ti/ss cathode [16,15]

The Ti coatings produced by VPS are able to protect the stainless steel BPPs decreasing significantly the material and fabrication cost of these components. These coatings can also be used to improve the mass properties of existing current correctors or to produce completely this component. The current collector of a proton exchange membrane electrolyzer consists of a porous structure of titanium such as a sintered disc, foams, felt or expanded meshes. However, the water or gas management faced by micro-structured current collector remains challenging in proton exchange membrane electrolysis. In PEM fuel cell technology, the problem of water management and contact resistance has been solved by the use of a backing layer which is applied to the gas diffusion layer [17,18]. Despite the improved performance on PEM fuel cells, none had been provided in terms of electrolyzers.

We developed a macro-porous layer (MPL) produced by VPS on the sintered Ti current collector of a proton exchange membrane electrolyzer. Fig. 8 presents the performance of an electrolysis cell with and without MPL. The inset shows a cross-section SEM image of the MPL deposited on the sintered Ti current collector. It can be observed, that the polarization curve of the cell with MPL has a lower slope than the one without MPL. The slope of the current potential curve is related to a ohmic drop caused by a decrease the contact resistance. At high current densities and consequently high gas production rates, the cell with MPL shows no mass transport limitation meaning an optimized mass transport behavior, while the cell with standard PTL increases rapidly the potential and a significant loss in efficiency is produced.

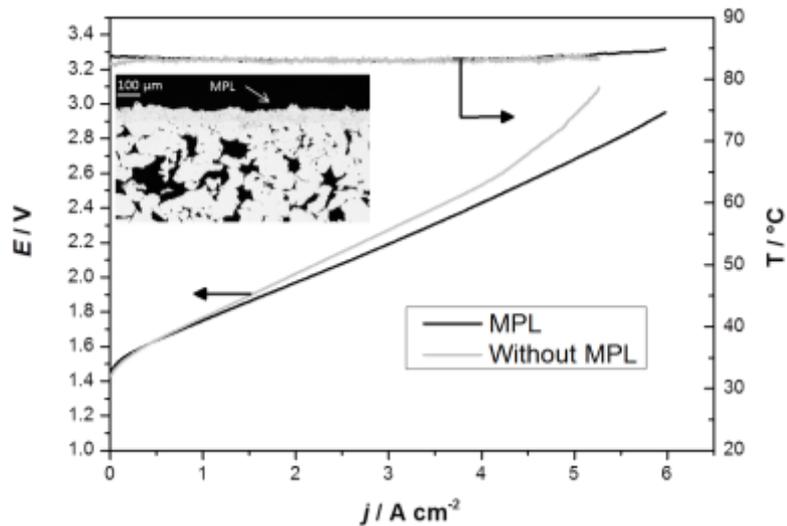


Fig. 8. Polarization curves up to 6 A cm^{-2} of PEM electrolyzer cells with and without MPL. The inset shows a cross-section SEM image of the MPL deposited on the sintered Ti current collector [19].

The mass transport properties of the MPL can be further improved by VPS coating technology and it can be applied on Ti meshes and other mechanically stable structures. Furthermore, by adjusting the thermal spraying parameters, it is possible to produce porous Ti layer without limitation of surface area by reducing the plasma enthalpy one is able to control the state of particle melting and produce highly porous structures. Some examples of different porous structures produced with various Ti particle sizes, number of sweeps numbers and plasma enthalpies are shown in Fig. 9.

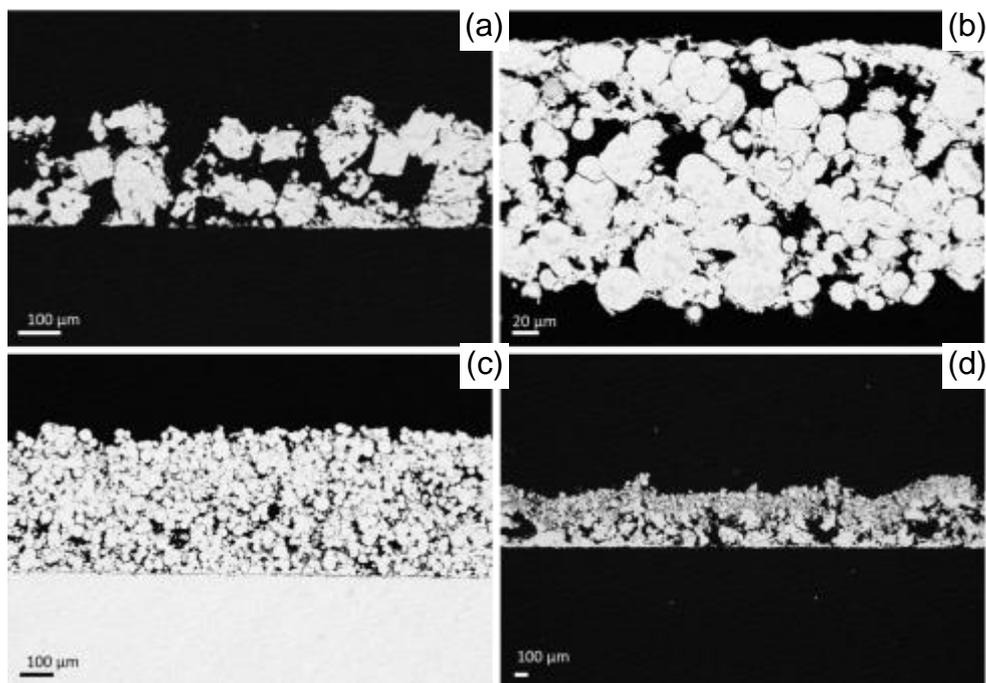


Fig. 9. SEM cross-section images of (a) freestanding porous layer of $125 \mu\text{m}$ Ti particles, (b) free-standing porous layer of $45 \mu\text{m}$ particles, (c) porous Ti layer with $45 \mu\text{m}$ particles on mild steel, as deposited. (d) Multi-functional layer with both particle sizes.

With VPS technology, thickness, porosity, pore size of the current collectors can be finely tuned to control important parameters such as capillary pressure, bubble point and tortuosity. The thermally sprayed current collectors reach the benchmark in terms of performance and the cost for large scale m²-size production is estimated in 20-100 USD m⁻² [14]. In overall, our results suggest the possibility of using thermal spraying for manufacturing the entire stack interconnector on a steel plate bipolar plate, that is from the protective Ti coating [15,14,13,16], to the large/medium pore size current collectors and backing layers [19]. All of them produced in fairly one manufacturing step, representing a cost reduction for the stack of almost 70 % [2].

Acknowledgements

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