**Table 2.** Reported examples of thermal spray feedstock materials and spraying routes explored to fabricate coatings relevant for water-splitting leading to hydrogen production.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Thermal spray process** | **Feedstock materials** | **Remarks** | **Coating thickness** | **Substrate** | **Ref.** |
| **Proton exchange membrane (PEM) electrolyser** | | | | | | |
| VPS | Ti (coating for bipolar plates) and thin layer of Pt using magnetron sputtering on top of Ti | Ti coatings can fully protect the stainless-steel bipolar plates, Pt layer can allow achieving a cell performance comparable to the baseline | Ti: 60 μm,  Pt: 1.8 μm | Stainless-steel | Gago et al. (2016)[97] |
| VPS | Ti (coating for bipolar plates) and thin layer of Pt using magnetron sputtering on top of Ti | Ti coatings can fully protect the stainless-steel bipolar plates, Pt layer can allow achieving a cell performance comparable to the baseline | Ti: 50-60 μm, Pt: 1.5 μm | Stainless-steel | Lettenmeier et al. (2017)[96] |
| VPS | Ti (coating for bipolar plates) and thin layer of Nb using magnetron sputtering on top of Ti | Ti coatings can fully protect the stainless-steel bipolar plates, Nb layer with superior corrosion protecting properties and stable behaviour in acid environment. Nb dense coating using VPS is possible; cell temperature: 38 °C | Ti: 50 μm, Nb: 1.4 μm | Stainless-steel | Lettenmeier et al. (2017)[98] |
| **Anion exchange membrane (AEM) electrolyser** | | | | | | |
| APS | NiAlMo (cathode), NiAl (anode) | Electrolyser can achieve a potential of 2.086 V at a current density of 2 A.cm–2; cell temperature: 60 °C; electrolyte: 1 M KOH | - | - | Wang et al. (2019)[99] |
| APS | Ni/C 80:20wt% (porous transport layer) | Novel approach for increasing performance in electrolysis by introducing a backing layer on a porous transport layer. Current density of 0.5 A cm−2 at operating voltage of 1.90 V | Ni/C 80:20wt%: 100 μm | Coated on top of a porous PTL made of stainless steel | Razmjooei et al. (2021)[100] |
| **Alkaline water electrolyser (AWE)** | | | | | | |
| Flame spray, APS | Ni, WC-12%Co | Improved electrocatalytic activities were related to increased surface area of electrodes and efficient release of hydrogen bubbles were related to sprayed surface roughness or unevenness | 25-150 µm | Steel (cathode) | Coker and Argade (1977)[101] |
| APS | Ni | The degree of coating oxidation was the main factor influencing the hydrogen evolution overpotentials at either the plasma-sprayed or sintered nickel cathode coatings; cell temperature: 80 °C; electrolyte: 30% KOH | - | - | Hall (1984)[102] |
| LPPS | Ni–Al | Decomposition potential of about 1.5 V was obtained; cell temperature: 180 °C | - | - | Henne, Schnurnberger and Weber (1984)[103] |
| VPS | Co3O4 spinel and Raney Ni/Co3O4 (for anodic oxygen evolution), Raney Ni and Raney Ni/Mo (for cathodic hydrogen evolution) | Cathode layers exhibited over voltages of 70 mV to 90 mV at 1 A cm−2 and 70°C in 25% KOH solution, whereas composite anodes (Raney nickel/Co3O4) showed overvoltage values of 290 mV at 1 A cm−2 | - | - | Schiller and Borck (1992)[104] |
| VPS | Mo-containing Raney Ni (for cathodic hydrogen evolution), Raney nickel/Co3O4 (for anodic oxygen evolution) | For the preparation of Raney Ni coatings, a precursor Ni-Al alloy was sprayed that had to be leached subsequently in caustic solution to remove the Al content, forming a porous, high-surface-area Ni layer | - | - | Schiller, Henne and Borck (1995)[105] |
| VPS | Ni-Al, Ni-Al-Mo | Ni-Al-Mo electrode was more active in 25% KOH, Ni-Al electrode was more active in 1M NaOH; cell temperature: 70 °C; electrolyte: 1M NaOH and 25% KOH | - | - | Miousse, Lasia and Borck (1995)[106] |
| Wire arc spray | Various Ni/Al ratios | Low over voltages were related to the high porosity of the deposited coatings; cell temperature: 25 °C; electrolyte: 1M NaOH | - | Mild carbon steel | Fournier, Miousse and Legoux (1999)[107] |
| VPS | Ti-Ru-Fe-O (2-1-1-2) (i.e., mixing by ball milling of Ti, TiO, Ru and Fe2O3) | Careful optimisation of the etching process could lead to the dissolution of all Ti2O3, leading to a high porous coating and can enhance electrochemical activity; cell temperature: 70 °C; electrolyte: Chlorate: NaClO3: 550 g/l, NaCl: 110 g/l, NaClO: 1 g/l, pH 6.5, adjusted with NaOH and HCl | - | Fe, Ti (with Ti/TiH2 interlayer) | Irissou et al (2002)[108] |
| VPS (high-frequency) | Ni—Al—Mo (NiAl5Mo2 (T), NiAl8Mo (G), NiAl7.5Mo1.5 (H), NiAl5Mo0.67 (I), 46%NiAl3 + 54%Ni2Al3 (B) and the mixtures 25–75% of T + B) | Increase in real surface area along with catalytic effect of Mo, the Ni—Al—Mo coated layers were more active than those prepared by alloyed powder (heating Ni and Al powders) with similar compositions; cell temperature: 25 °C; electrolyte: 1 M KOH | - | - | Birry and Lasia (2004)[109] |
| Wire arc spray | Ni-Al, NiTi-Al | Increased activity for the hydrogen evolution reaction is due to an increased real surface area in case of the skeleton Ni electrodes and to the catalytic effect of Ti in case of the skeleton NiTi electrodes; cell temperature: 25 °C; electrolyte: 1M NaOH | - | Steel | Kellenberger et al (2007)[110] |
| APS | Raney Ni (Ni-Al (50:50)) | Best electrocatalytic activity towards HER was obtained for 100 μm thick coated electrode, with 96% efficiency at 300 mA cm−2 current density and 70 °C, attributed to very high electroactive area and enhanced kinetics on sprayed surface; cell temperature: 30-80 °C; electrolyte: 30% KOH | 30, 100, 300 µm | Raney nickel | Chade et al (2013)[111] |
| APS (Ni), SPS (NiO) | Ni, NiO | Higher surface areas were observed for all SPS deposits compared to those deposited using APS, attributed to the formation of fine porous agglomerates on the surface of the SPS coatings; electrolyte: 0.5M NaOH | - | Carbon steel | Aghasibeig et al (2014)[113] |
| APS (Ni), SPS (NiO) | Ni, NiO | Addition of submicron-sized cauliflower-like aggregates by SPS on the rough and porous surface of the APS deposited coatings significantly increased the exchange current density and improved the electrocatalytic activity of the electrodes; electrolyte: 1M NaOH | 100 µm (APS); 10-40 µm (SPS) | Inconel | Aghasibeig et al (2016)[114] |
| APS | Raney Ni, Ni–Al | Through hydrogen and temperature heat treatment of the electrode, an enhancement in the uniformity of Al distribution as well as adhesion of the coating to the substrate was observed; electrolyte: 1 M KOH | - | Ni | Kim et al. (2018)[115], Kim et al. (2019)[116] |
| **Solid oxide water electrolyser (SOWE)** | | | | | | |
| APS (Al2O3), Flame spray (Ni), Low pressure APS (YSZ), flame spray (calcium or strontium-doped LaCoO3 or strontium-doped LaMnO3), APS (Ni-Al) | Al2O3 (for sealing & preventing oxidation), Ni (cathode), YSZ (electrolyte), calcium or strontium-doped LaCoO3 or strontium-doped LaMnO3 (anode), Ni-Al (interconnect) | Tubular cell design; cell temperature: 950 °C; electrolyte: YSZ | Al2O3: 100 µm, Ni: 80 µm to 110 µm, YSZ: 100 µm, calcium or strontium-doped LaCoO3 or strontium-doped LaMnO3: 200 µm to 150 µm, Ni-Al: 250 µm | - | Hino et al. (1997)[117] |
| APS | LSM (La0.8Sr0.2MnO3) and LSCF (La0.6Sr0.4Co0.4Fe0.6O3) (cathodes), NiO+YSZ (fuel electrode), 9 mol% YSZ (electrolyte) | LSCF showed enhanced electrochemical performance compared to cells with LSM. Water splitting voltage was reduced to 1.4 V at an operating temperature of 800 °C and to 1.28 V at 850 °C; cell temperature: 800 °C; electrolyte: 9 mol% YSZ | NiO+YSZ: 50 µm, 9 mol% YSZ (40 µm), | FeCrMnTi | Ansar et al. (2008)[118] |
| APS (anode, cathode), VPS (electrolyte) | Ni/YSZ (cathode), YSZ (electrolyte), LSCF (anode) | Cell voltage during electrolysis operation at a current density of −1.0 A cm−2 was 1.28 V at an operating temperature of 850 °C and 1.4 V at 800 °C; cell temperature: 800-850 °C; electrolyte: YSZ | Ni/YSZ: 50 µm, YSZ: 40 µm, LSCF: 30 µm | Porous ferritic steel | Schiller et al. (2009)[119] |
| APS, screen printing | Ni (bond layer) (steam/hydrogen side of separator plate), scandia-stabilized zirconia (electrolyte), strontium-doped manganite (anode), manganite-zirconia (inner layer), pure manganite (middle layer), cobaltite (outer bond layer), nickel-zirconia (cathode) | Demonstrated straightforward scalability of the high temperature electrolysis for long term operation and hydrogen production; cell temperature: 800-850 °C; electrolyte: scandia-stabilized zirconia | Ni: 10 µm, Scandia-stabilized zirconia: 140 µm, manganite-zirconia: 13 µm, pure manganite: 18 µm, nickel-zirconia (13 µm) | Stainless steel (interconnect) | O’Brien et al. (2010)[59] |
| APS | Ni/NiO 50%–YSZ 50% (support electrode layer), Ni/NiO 25%–YSZ 75% (electrolyte transition layer), YSZ 100% (electrolyte), 50% YSZ–50% LSM (electrolyte-end transition layer), LSM 100% (end electrode) | Fabrication of free-standing solid oxide cells exclusively by APS thermal spray without the need of using any porous metallic support; electrolyte: YSZ | Ni/NiO 50%–YSZ 50%: 300–350 μm, Ni/NiO 25%–YSZ 75%: 100–120 μm, YSZ 100%: 100–120 μm, 50% YSZ–50% LSM: 80–100 μm, LSM 100%: 70–90 μm | - | Vardavoulias et al. (2021)[120] |
| **Thermochemical water splitting (TWS)** | | | | | | |
| HVOF | YSZ, Al2O3,Diamalloy 4006 (bond coat) | Inconel 625 substrate performed better than stainless steel AL6XN substrates; electrolyte: molten CuCl | 70 µm (YSZ); 70 µm (Al2O3) | Inconel 625, super austenitic stainless steel or AL6XN | Siantar (2012)[58] |
| HVOF (for Diamalloy 4006) | YSZ, Diamalloy 4006 (bond coat) | YSZ coating with Diamalloy 4006 bond coat can provide better protection to the underlying base metal than only YSZ layer; electrolyte: molten CuCl | - | Medium carbon steel (1045) | Azarbayjani, Rizvi and Foroutan (2016)[121] |
| HVOF, APS | Diamalloy 4006 (bond coat), super hard steel 9172 (bond coat), Al2O3, YSZ | Porosities less than 1% should be tested in order to shield the substrate from the harsh CuCl environment; electrolyte: molten CuCl | - | - | Azhar (2016)[122] |
| HVOF (for Diamalloy 4006) | YSZ, Diamalloy 4006 (bond coat)+YSZ | Diamalloy 4006 with YSZ or Al2O3 top coating survived longer exposure to molten CuCl; electrolyte: molten CuCl | - | Medium carbon steel (1045) | Naterer et al. (2019)[46] |
| **Photolysis water splitting (PWS)** | | | | | | |
| APS, HVOF | TiO2 | - | - | - | Chen, Jordan and Gell (2008);[125] Mauer, Guignard and Vaßen (2013);[126] Zhang et al. (2013);[127] Dosta et al. (2016);[128] Wang et al. (2015);[129] Robinson et al. 92015);[130] Kumar et al. (2016);[131] Khatibnezhad et al. (2021);[132] |
| APS | ZnO |  | - | - | Navidpour et al. (2017)[80] |
| **Photoelectrochemical (PEC) water splitting** | | | | | | |
| APS | ZnFe2O4:Fe2O3 | Solar-to-hydrogen conversion efficiency of 1.25% under simulated solar radiation with a hydrogen evolution rate of 99 μmol h−1; electrolyte: 1 M NaOH | 10 µm | Stainless steel | Dom et al. (2013)[133] |
| Cold spray | Cu2O, CuO | Photocurrent densities of up to 3.1 mA/cm2; electrolyte: 1 M KOH | - | Indium tin oxide (ITO)-coated soda lime glass | Lee et al. (2016)[134] |
| Cold spray | WO3, TiO2 | Highest photocurrents were observed for WO3 photoelectrodes in the potential range of 0.6–1.6 V, for TiO2 photoelectrodes in the low potential range from 0.0–0.6 V; electrolyte: electrochemical testing: 0.1 M KCl; Photoelectrochemical testing: 0.5 M (H2SO4) | - | Ti | Haisch et al. (2017)[137] |
| Cold spray | Fe2O3 (followed by coating with ZnO and then TiO2 overlayers using atomic layer deposition technique) | Photocurrent of Fe2O3 films (0.5 mA cm−2) improves significantly, to 4.25 mA cm−2, after their surface modification with an ultrathin ALD-based ZnO/TiO2 coating; electrolyte: 1 M NaOH | - | Indium tin oxide (ITO) | Kim et al. (2019)[138] |

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