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Review paper

Thermal spray coatings in batteries, electrolyzers and solid oxide electrochemical systems

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Abstract

Energy systems based on electrochemically active materials frequently suffer from poor performance and limited lifetimes due to interfacial problems that can be mitigated by micro- to nanoscale structuring with thermal spray coatings (TSC). This review synthesizes existing knowledge and develops a process-structure-property framework that uniquely links TSC process parameters to the coating microstructure and interfacial chemistry across different electrochemical systems, with a focus on innovative cross-system design principles. This review covers various TSC technologies (atmospheric plasma spray, suspension plasma spray, high-velocity oxy-fuel, and cold spray) with reference to their ability to control porosity and phase distribution. These process parameters affect ion or electron conduction, interfacial resistance, and mechanical stability. The issues of transport limitations caused by porosity, inter-splat bonding, and non-equilibrium phase transformations were studied. Functionally graded interfaces, adaptive coating systems, and machine learning-based process development are innovative approaches investigated to achieve defect-tolerant functional interfaces. This study offers guidelines for designing next-generation TSC that are more durable, scalable, and exhibit better electrochemical properties, thereby improving the performance and lifespan of electrochemical energy systems. The battery, proton exchange membrane, alkaline fuel cells and solid oxide fuel cell/solid oxide electrolysis cell systems were analysed with respect to one another to establish general process-structure-property relationships for electrochemical interfaces.

Keywords

Electrochemical energy systems; coating processes; electrodes; interfacial engineering; microstructural features; splat bonding; porosity; AI-assisted materials design; electrochemical stability

Introduction

Batteries, electrolyzers, and solid-oxide cells are key technologies for developing sustainable energy systems. Despite rapid progress, their efficiency and lifetime are largely limited by transport losses and chemical and mechanical degradation rather than intrinsic properties. Therefore, interface engineering has become a key approach for enhancing the performance, durability and safety of these devices [1-5]. Thermal spray coatings (TSCs) provide a scalable and flexible platform for interface engineering by allowing control over the microstructure, porosity, phase, and residual stress. TSC processes enable the high-speed deposition of thick and functional coatings with desired structures, making them suitable for large-scale and complex applications. Through careful manipulation of process variables, including particle temperature, velocity, well-designed transport pathways, and stable interfaces, TSC processes can be achieved [6-10]. Although there are many studies on thermal spray coatings (TSCs) for specific electrochemical technologies, the literature remains highly fragmented, and most studies have focused on TSCs used in batteries, electrolyzers, or solid oxide electrochemical systems. However, a comprehensive understanding of the effect of thermal spray process parameters on the microstructure, interfacial characteristics, transport behaviour and the long-term electrochemical performance of coatings for these energy systems remains to be developed. In addition, there has been a lack of interest in the identification of common degradation mechanisms and transferable coating design principles that can be used in different electrochemical platforms.

The main purpose of this review is to compare and assess the application of thermal spray coatings in batteries, proton exchange membrane (PEM) electrolyzers, alkaline electrolyzers, and solid oxide fuel cell/solid oxide electrolysis cell (SOFC/SOEC) systems from a process-structure-property approach. The review systematically characterizes and analyses the effect of various major thermal spray technologies (*i.e.* atmospheric plasma spraying (APS), suspension plasma spraying (SPS), high-velocity oxy-fuel spraying (HVOF), vacuum plasma spraying (VPS) and cold spraying) on coating architecture, porosity, phase distribution, interfacial resistance and mechanical integrity. Furthermore, the review identifies the most common degradation phenomena, coating design approaches, function-graded architectures and new trends like artificial intelligence-optimized processes. This review aims to offer guidelines for the development of durable, scalable, high-performance, thermal spray coatings for next-generation electrochemical energy systems by establishing generalized relationships among coating processing, microstructure evolution and electrochemical performance.

Thermal spray coatings in electrochemical energy devices

TSC are increasingly utilized in energy storage and electrochemical systems, including batteries, electrolyzers, and solid oxide fuel cells (SOFCs). Nickel-cobalt-chromium alloys are used to make coatings that increase electrode stability by forming a protective layer that reduces degradation during charge-discharge cycles. The use of ceramic materials such as Al_2O_3, TiO_2, and ZrO_2 helps retain capacity by preventing unwanted side reactions at the electrode-electrolyte interface. The use of carbon coating on electrodes helps construct the electrode surface, extending electrode lifetime by enhancing the electrode's electrical conductivity and structural strength under repetitive cycling conditions. The use of these coating materials can decrease the chances of electrode corrosion in the battery and help prolong its lifespan. These coatings help achieve uniform lithium-ion diffusion, resulting in improved electrochemical performance and minimizing capacity fading over time [11].

TSC techniques enable precise material layering and structural control, enhancing the stability, efficiency, and longevity of energy storage applications, thus driving advancements in sustainable and reliable energy technologies [12-15].

Comparative role of different thermal spray coating processes

Atmospheric plasma spraying (APS) is the most frequently used TSC in electrolysis, and its flexibility and low cost are attributed to the formation of functional electrode layers. Its applicability has been demonstrated in alkaline and proton-exchange membrane (PEM) systems [16]. Vacuum plasma spraying (VPS) is a technology used to create high-quality coatings [17]. Suspension plasma spraying (SPS) is a TSC method that uses sub-micrometre particle suspensions as the feedstock. The result of this microstructural refinement is a dense yet porous electrode coating that is optimal for solid-oxide fuel cells (SOFCs). Cathodes of LaSrMn perovskites manufactured by SPS exhibited better electrochemical characteristics owing to their customized microstructure [18].

Table 1 shows that TSC is important for manufacturing electrochemical energy equipment. This facilitates scaling, saves money, and improves performance. The broad application of TSC technologies in alkaline electrolyzers, proton exchange membranes (PEM), and solid oxide electrolysis cells (SOECs) should be considered [19-26].

Table 1. *Comparative role of TSC across batteries, electrolyzers and SOFC/SOEC systems*

Technology/method	Process variables	Battery application	Key function	Opportunities
APS, VPS, HVOF, SPS	T: 2000-3200 K V: 150-600 m s^{-1} SD: 80-150 mm	Cathode/anode coatings; solid-state interfaces	Tunable porosity and transport pathways	Scalable, multi-material coatings [19]
SPS, HVOF, Cold spray	d_p: 0.1-5 µm V: 200-1200 m s^{-1}	3D porous electrodes	High-surface-area transport architectures	High-surface-area, cost-effective electrodes [20]
Vacuum plasma spraying (VPS)	P: 1-20 kPa T: 2200-3000 K V: 300-700 m s^{-1}	Bipolar plate coatings	Dense conductive and corrosion-resistant interfaces	Low-cost bipolar plates [21]
Spray + sintering	T: 2000-2800 K Sintering: 1100-1400 °C t: 1-5 h	Solid-state electrolytes; separator coatings	Dense ion-conductive layers	Dense electrolyte fabrication [22]
Multi-technique spraying	T: 1800-3200 K V: 200-800 m s^{-1} FR: 10-50 g min^{-1}	Functionally graded electrodes	Graded multifunctional interfaces	Process optimization, graded coatings [23]
Atmospheric plasma spraying (APS)	Plasma T: 10,000-15,000 K V: 100-300 m s^{-1}	Ni-based catalytic coatings	Enhanced electrochemical activity	Noble metal replacement [24]
Liquid precursor HVOF (LP-HVOF)	Flame T: 2500-3200 K V: 500-900 m s^{-1}; FR: 5-20 mL min^{-1}	Nanostructured cathode coatings	Fine-structured transport coatings	High-performance cathodes [25]
HVOF	V: 500-900 m s^{-1}; T: 1800-2600 K; SD: 150-300 mm	Porous transport layers	Strong adhesion with controlled porosity	Improved mass transport layers [26]

T = particle/processing temperature; V = particle velocity; P = chamber pressure; FR =feed rate; SD= stand-off distance

High-temperature electrochemical systems require coatings that can maintain interfacial stability, conductivity, and corrosion resistance under aggressive operating conditions. TSC are increasingly being explored for such applications owing to their scalable deposition and tuneable microstructures. Interfacial transport losses and degradation reactions, rather than bulk material behaviour, are the major limitations of electrochemical energy systems [27-29]. Metallic finishes are used to ensure that the electric paths remain clear and to prevent an increase in the contact resistance. Moreover, graded or composite coatings help reduce thermal expansion discrepancies and mechanical stress buildup, thereby reducing crack generation and gas crossover [30-33].

Although originally developed for SOFC and electrolysis applications, these transport and interfacial design principles are increasingly transferable to advanced-battery systems. However, it also includes water electrolysis and solid-oxide cells. This is because they degrade in a similar manner, and this can be treated by applying a TSC. In these electrochemical technologies, performance decline is typically caused by corrosion, gaseous permeation, increased contact resistance, and thermomechanical mismatch during cycling [34-36]. Similar protection strategies, such as dense ceramic coatings, metallic bond coatings, graded interfaces, and conductive protective coatings, are used to control the transport processes and stabilize the reactive interfaces [37-39]. This review primarily focuses on battery-related TSC while incorporating insights from PEM electrolyzers and SOFC/SOEC systems, in which similar interfacial degradation and transport phenomena govern electrochemical performance. Cross-system comparisons were used to establish generalized coating design principles.

Fundamental principles of thermal spray coatings in electrochemical energy systems

TSC involves applying molten or semi-molten particles onto surfaces to form functional layers that enhance wear and corrosion resistance and interfacial properties. For battery interfaces that require strict control over the mechanical, chemical, and electrochemical properties, understanding the underlying principles of TSC finishes is crucial for achieving maximum functionality and durability. Consequently, lessons from electrolysis and solid oxide systems can be directly applied to battery interface design by reducing interfacial resistance, maximizing transport continuity, and eliminating degradation pathways [40-42]. TSC deposition rapidly solidifies molten or semi-molten particles that strike a substrate, spreading and forming lamellar splats that combine to form a hierarchical microstructure of splats, boundaries, pores, and microcracks. While typical bonding ratios reach approximately 32 %, controlling the substrate or coating surface temperature before impact can increase bonding to nearly 100 %, producing denser and more coherent coatings [43].

Table 2 shows that the use of TSC in batteries, electrolyzers, and solid-oxide systems involves similar transport processes. This allows coating design techniques to be shared across these areas [44-47].

Table 2. *Cross-system mapping of transport mechanisms, interfacial degradation, and coating design principles in electrochemical energy systems*

Transport mechanisms	Batteries (LIB/SSB)	Electrolysis (PEM/alkaline)	SOFC/SOEC	Common role of coating
Ion transport	Li^+ diffusion across SEI/CEI	H^+ / OH^- transport	O^{2-} transport	Controlled by porosity & phase [44]
Interfacial resistance	Electrode-electrolyte impedance	Bipolar plate/contact resistance	Electrode-electrolyte junction	Reduced *via* splat bonding [45]
Degradation	SEI breakdown, dendrites	Corrosion, oxidation	Phase instability, coarsening	Suppressed *via* protective layers [46]
Mechanical failure	Particle cracking	Thermal stress cracking	Thermal mismatch cracking	Mitigated *via* graded coatings [47]

Degradation mechanisms of thermal spray coatings

Sufficient melting and high impact velocity enhance spreading, interfacial contact, and bonding, producing dense, low-defect coatings. Conversely, insufficient melting or oxidation leads to incomplete spreading, weak cohesion, and porous microstructures [48].

Figure 1 depicts some common interfacial degradation mechanisms of batteries, PEM electrolyzers, and SOFC/SOEC systems. These include stresses that degrade interfaces, such as chemical, mechanical, and electrochemical stresses, leading to performance loss. Understanding of these elementary mechanisms will assist in developing long-term approaches to coatings and interface engineering to extend and enhance the performance of a range of electrochemical energy devices [49,50].

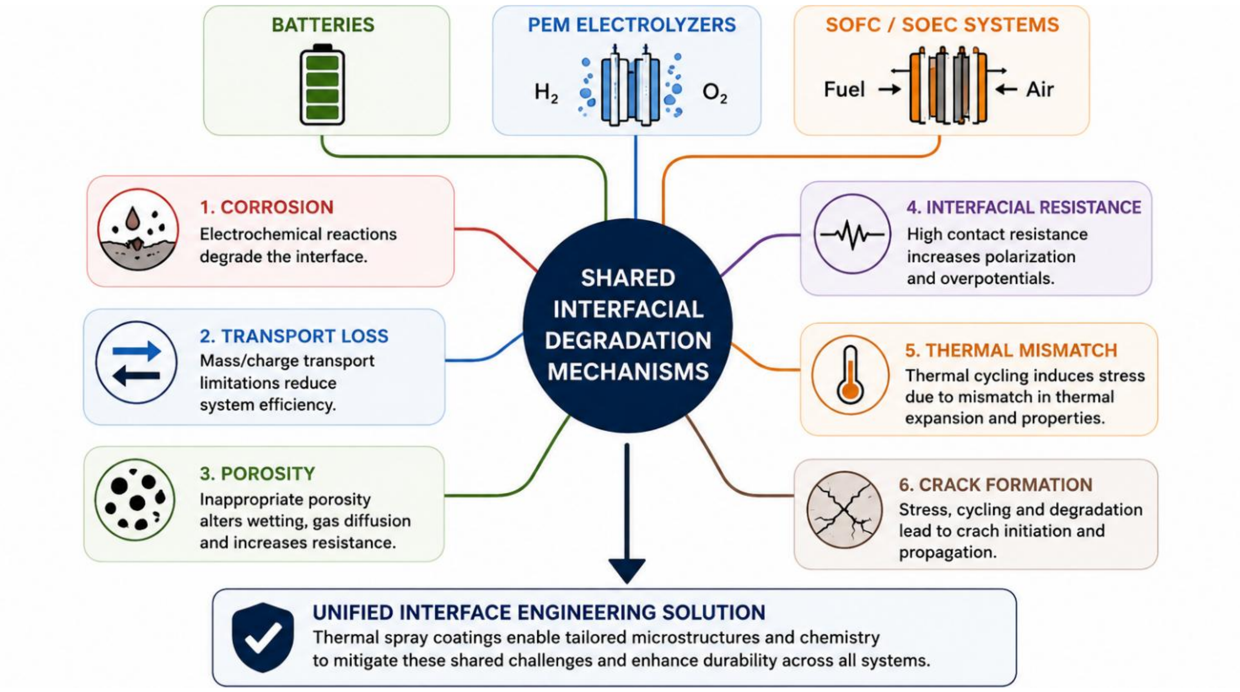

Figure 1. *The shared interfacial degradation mechanisms across batteries, PEM electrolyzers and SOFC/SOEC systems*

The interfacial resistance between the coating and substrate, as well as between the splats, is one of the most prevalent constraints in electrochemical devices. Continuous contact networks across splats form the basis of electrically conducting pathways and are extremely sensitive to bonding quality and defect density. Interfaces with strong bonds and minimal oxide inclusions exhibit low contact resistance and long-term stability, whereas weak or oxidized bonds cause conduction breaks, increase polarization, and reduce efficiency [51,52].

As shown in Figure 2, the closer the temperature of the spray particles was to their melting point, the more the particles tended to spread and adhere to the surface.

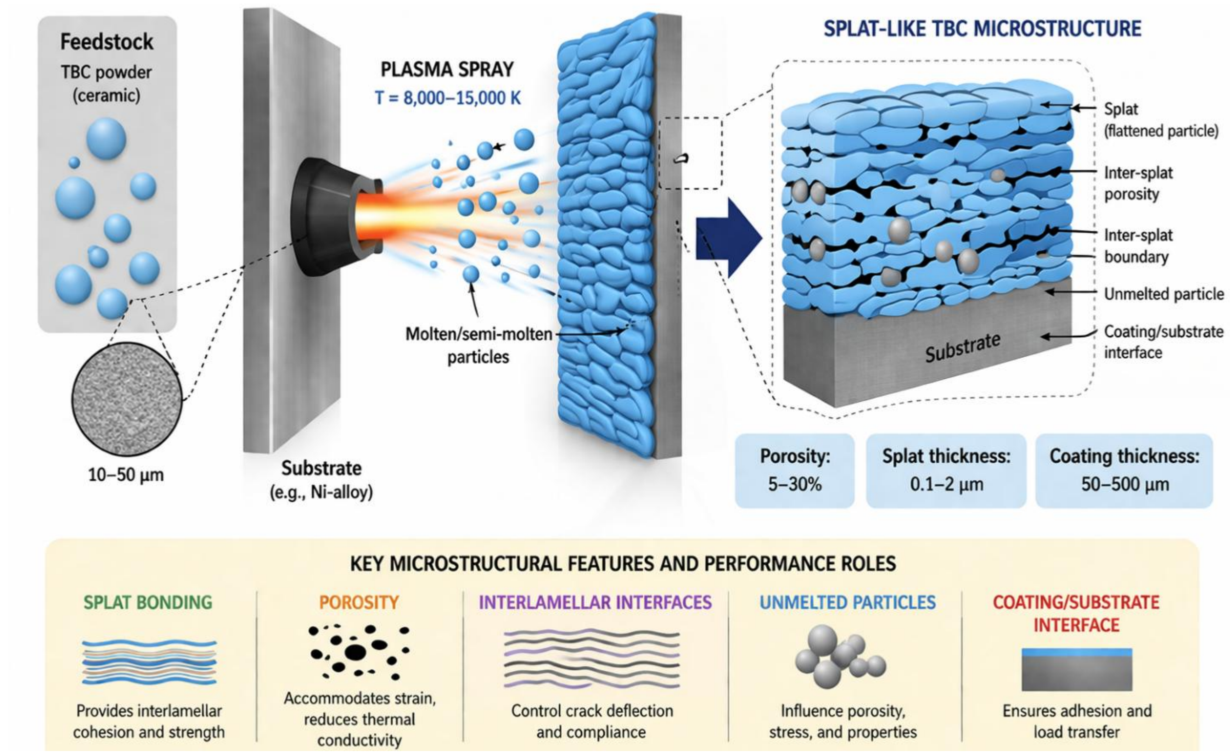

Figure 2. *Splat-based microstructure formation during plasma spraying, illustrating inter-splat boundaries, pores and microcracks [54] (CC BY 4.0 Attribution)*

This enhanced the quality of the coating and made it denser. Semi-molten particles can protect molten particles, prevent complete filling of the cavity, and increase porosity. To achieve this, the melting velocity and spray conditions of the particles must be controlled. This facilitates the balancing of the degree of material adhesion, porosity, and cross-lamination resistance [38].

Process-structure-property relationship for thermal spray coatings

The process-structure-property relationships of TSC are also strong and need to be strictly regulated according to the application demands. Yttria-stabilized zirconia (YSZ) coatings can be designed to be highly porous, thermally resistant, or highly dense and gas-proof, similar to a solid oxide cell (SOC) electrolyte. The same control is required in battery systems to modify the coating for purposes such as ion-conductive layers and protective barriers. This control requires close monitoring of the spray parameters, including plasma energy, spray distance, material to be used, and surface state [53].

Multilayer and functionally graded architectures also improve the performance of coatings by alleviating thermal expansion mismatches and reducing stress concentrations at interfaces. Compositional or structural transitions are achieved gradually, leading to increased adhesion, decreased crack propagation, and increased longevity during thermal and electrochemical cycling. These architectures are most applicable to battery and solid-state systems, where interfaces between different mechanical and chemical systems can result in rapid degradation [55-57].

Dense structures are preferable for SOFC electrolytes because they facilitate ion transport and prevent gas passage. TSCs are produced by projecting hot particles onto surfaces. These particles dissipate, cool quickly, and adhere to surfaces. The density of the coating, holes, and resistance depended on the extent to which the particles melted and adhered. These factors must be adjusted to make the coatings suitable for specific applications. TSC can be modified to assume different structures, which help it suit different industry needs, such as heat retention or facilitating chemical reactions. Zirconia-yttria (YSZ) is a popular electrolyte material because it effectively conducts ions at room temperature. It is usually combined with lanthanum strontium manganite (LSM) to form density- and porosity-balanced structures [58,59].

To prepare a solid oxide cell (SOC), one must follow two steps, as indicated in Figure 3 (top). The second step involves adding layers to a base, which forms a self-supporting cell. The image below shows how the layers are stuck together. These layers, labelled a-e, were approximately 10 to 50 µm thick and included support, transition, electrolyte, transition, and electrode. The varying layering formulas aid in minimizing heat and mechanical problems. The gases were prevented from passing through the thick YSZ electrolyte. This architecture leverages the TSC method to deposit thick, functionally graded surfaces (FGS) in a single, scalable process [60].

Non-equilibrium phases, phase segregation, and residual stresses that may arise from the rapid solidification of TSC can also significantly affect coating performance. Although these properties can be useful in some applications (*e.g.* metastable phases with better catalytic performance), they frequently require post-processing or careful parameter control to guarantee their phase stability and reproducibility. Moreover, it is difficult to obtain consistent coatings across complex geometries [61]. The effectiveness of the therapeutically sprayed coating on the battery systems was analysed using a model. This involves the sticking together of particles, the extent of the amount of empty space, and the distribution of various phases. These considerations affect the flow of the material, its stability, and wear over time.

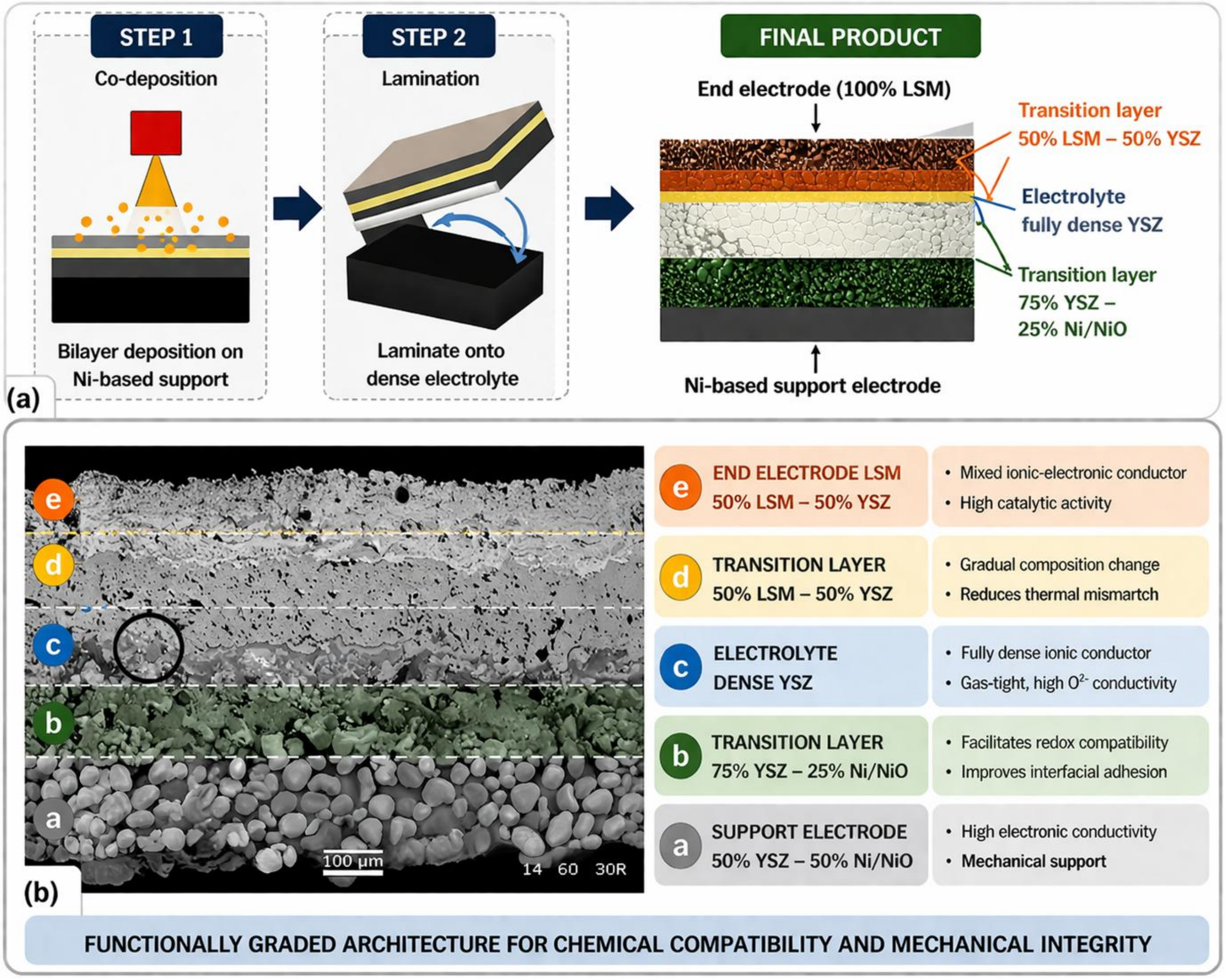

Figure 3. *FGS ceramic structures formed by TSC, which are promising for solid-oxide cell applications [60] (CC BY 4.0 Attribution)*

Applications of thermal spray coatings in batteries

TSC is a useful method for improving the performance of battery systems. With TSC technology, cells can be produced without the time-consuming sintering steps [62,63]. TSC technologies are promising for membrane manufacturing because these coatings often contain microcracks and pores. As this paper will show, it is indeed possible to achieve the targets and obtain high-performance data from the cells. These cells had porous ferritic steel substrates that could attain a power density of 0.8 W cm^{-2} [64,65]. TSC methods are useful for applying coatings on a large scale. Techniques such as atmospheric plasma spraying (APS), high-velocity oxygen fuel (HVOF) and suspension plasma spraying (SPS) are used to create coatings with specific porosities and structures. This improves the movement of the ions and electrons. Unlike other methods, TSC quickly produces thick or layered coatings that adhere well and are robust. New methods have been developed for creating dry-spray electrodes. These electrodes exhibit better bonding, strength, and durability [66-68]. Nevertheless, they are not widely applicable due to numerous technical barriers, such as low electrolyte conductivity, dendrite growth, and limited cycling/rate performance [69]. The surface affects the performance of the battery over time. Oxide-based coatings are often used to create protective layers on metal surfaces. These layers separate the electrode from the electrolyte and maintain the ionic conductivity [70]. The effectiveness of these coatings depends on their thickness, structure, and defect characteristics. These factors influence the movement of Li^+ ions and the resistance at the surface. It has been found that the activation barrier to Li hopping is strongly dependent on the size of the tetrahedral [71].

Al_2O_3 coatings can effectively inhibit lateral reactions between the cathode and the electrolyte, which is one of the main causes of capacity fading in LiBs. Ni-rich $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathodes, a layer of Al_2O_3 avoids direct contact with the electrolyte, improving capacity retention to 81.8 % at 25 °C and 68.5 % at 55 °C [72,73]. The Al_2O_3 film has been shown to maintain the structural integrity of cathode materials, such as $LiFePO_4$ and lithium- and manganese-rich oxides, by eliminating direct contact between these materials and the electrolyte and minimizing cell impedance. These coatings improve the structure and maintain capacity, especially at high voltages above 4.3 V and temperatures above 50 °C. Some experiments indicate that the coatings might also scavenge acidic species in the electrolyte, which contributes to their protective properties [74-76].

In addition to Al_2O_3 systems, coatings such as TiO_2, ZrO_2, and WO_3 offer additional benefits to substrates. They provide mechanical support and chemical stability to the cells. For instance, TiO_2 on Si-based anodes allows them to expand during use, which keeps them strong and stable. ZrO_2 coatings improve compatibility and prevent electrolyte breakdown [77-79].

Figure 4 shows how a lithium-ion battery (LIB) charges and discharges during each cycle. To develop safer and better batteries, it is necessary to gain profound insight into the reactions that alter battery components and the mechanisms by which they occur. It also focuses on the movement and reactions of lithium ions at the surface during usage. The text explains how surface coatings affect the stability and movement of Li^+ ions [80].

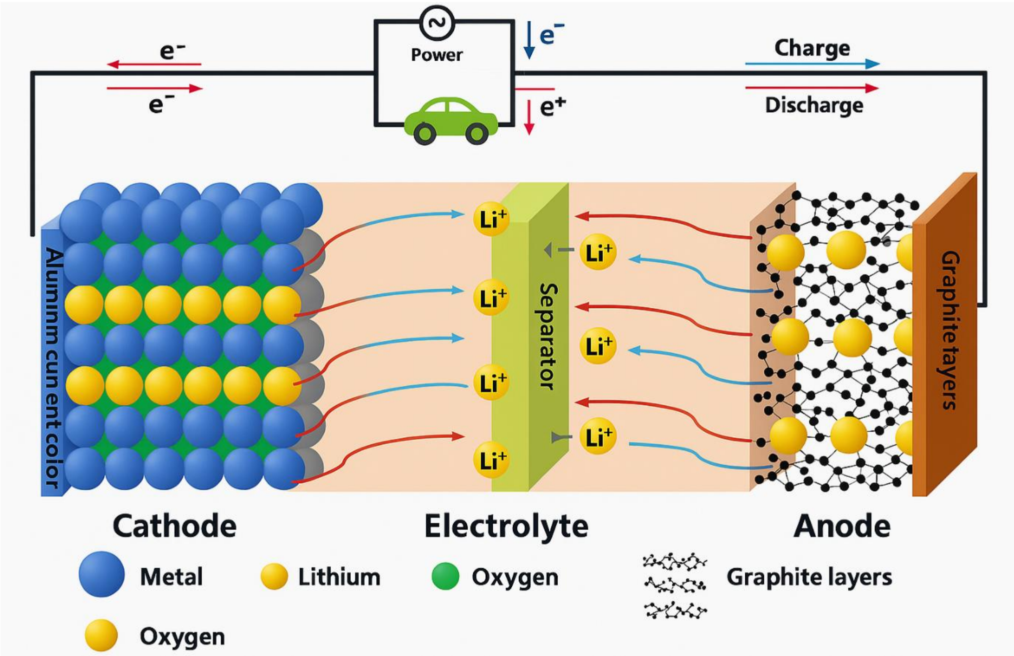

Figure 4. *Schematic illustration of the charge/discharge principle of a LIB cell [80] (CC BY 4.0 Attribution)*

The performance of $LiMn_2O_4$ (LMO) and its aluminium-coated version (LMO@Al) has been extensively studied to improve the stability and capacity of lithium-ion batteries (LIBs) [81]. Al_2O_3-coated $LiMn_2O_4$ lasts longer because it prevents dissolution and reduces surface resistance [82]. Lithium metal electrodes have problems, such as slow lithium migration and the formation of gaps during use, which limit their power. Next-generation energy storage devices include high-energy-density lithium metal batteries (LMBs). Nevertheless, the 55 °C rolled growth of dendrites and the enormous volume change restrict their practical use. Nevertheless, the uncontrolled growth of lithium dendrites and the large volume expansion of lithium metal during cycling remain major challenges that limit the practical implementation of lithium metal batteries. A new Mg-doped Li-LiB alloy with a three-dimensional (3D) LiB structure was introduced. This structure is formed during the process and is called the Li-B-Mg composite. This helps prevent the formation of Li dendrites and reduces volume changes [83]. The self-diffusion of Li in pure Li metal is too low to sustain high current densities, leading to the formation of voids at the interface with solid electrolytes [84]. These improvements arise from controlled interfacial chemistry and optimized Li^+ transport across the coating layer, which are governed by the coating thickness, phase structure, and defect density.

Figure 5 shows the movement of lithium and the change in the surface when stress was applied. It compares (a) a pure lithium metal electrode and (b) a Li-rich Li-Mg-alloy electrode. In both cases, ξ is the distance from the back of the electrode, C_{Li} is the amount of Li in a specific area, and L is the total thickness of the alloy, respectively. For pure lithium metal (a), the diffusion of vacancies and adatoms results in a narrow structural relaxation zone of thickness ξ_0 near the active interface. The presence of non-equilibrium defects and pores within a rapidly lithium-depleted surface results in a steep concentration gradient between C_0 and C_{Li} at the front. These flaws result in surface roughening and dendrite development. In contrast, the Cd-Li Mg alloy electrode (b) exhibits chemical (bulk) diffusion, which balances the concentration gradients across the electrode [85].

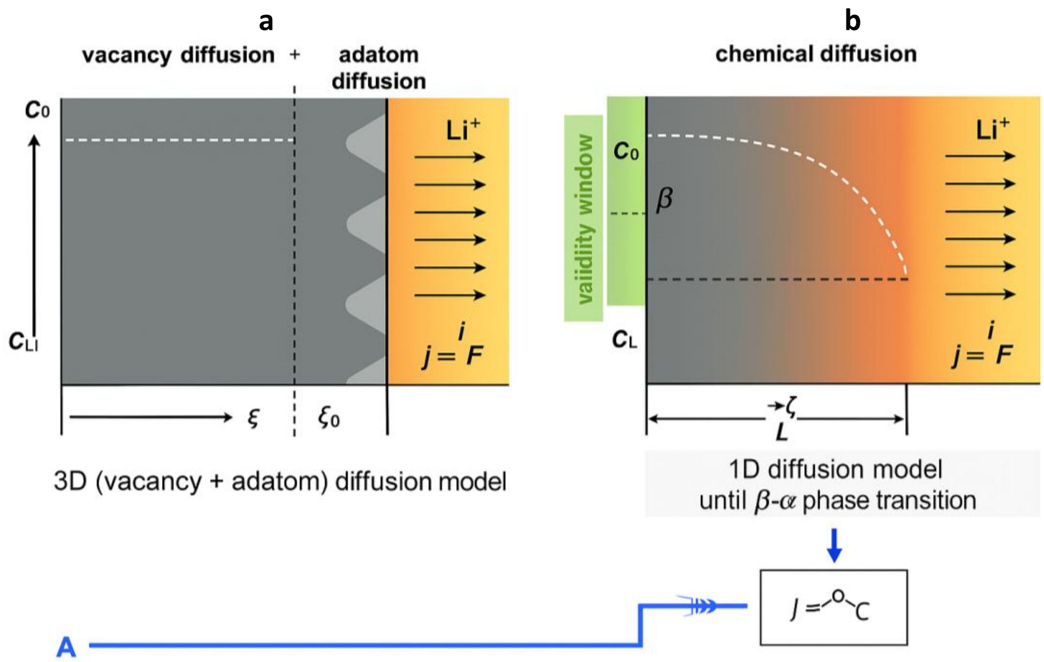

Figure 5. *Diagram showing how lithium moves and how the surface changes for a) a lithium metal electrode and b) a lithium-rich Li-Mg alloy electrode when a positive charge is applied [85] (CC BY 4.0 Attribution)*

The interaction between lithium metal and solid electrolytes can be improved by using layers that facilitate lithium migration and prevent dendrite growth. The interfaces were demonstrated to be induced by $Zn(NO_3)_2$. Atomic layer deposition was used to add an Al_2O_3 coating to the electrodes. In this case, the Al atoms of the precursor occupied sites on the LMO surface, thereby reducing the oxidation of Mn ions and enhancing the electrochemical capacity [86].

The modification of $LiMn_2O_4$ (LMO) surfaces with Al_2O_3 surface layers has been proven to significantly increase the electrochemical stability by inhibiting interfacial lateral reactions and reducing Mn dissolution [87,88].

Conformal and hybrid coatings are important for all-solid-state battery applications. They help stabilize solid-solid interfaces, where mechanical mismatches and interfacial resistance often cause problems. Ion-conductive coatings, such as $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$, *i.e.* lithium aluminium germanium phosphate (LAGP), provide stable layers that allow lithium-ion passage. These layers prevent unwanted interfacial reactions without reducing ion mobility [89-91].

Challenges and limitations of thermal spray coatings

Although coating technologies have progressed, there are still some important challenges to overcome to optimize coated battery components and bring them to market. The presence of microstructural defects within the coatings (cracks, voids and uneven grain structures) can significantly affect the electrochemical performance, allowing for unwanted side reactions or obstructing the movement of ions and electrons.

Coatings need to be uniformly and permanently attached to carbon fibres without degrading the mechanical properties of the carbon fibre and improve or maintain electrochemical properties. To solve these complex problems, the development of reliable, high-performance batteries is crucial for next-generation energy storage applications [92].

Three coupled mechanisms can be used to rationalize the dominant failure modes: (i) porosity-induced transport constraints, (ii) interfacial bonding constraints, and (iii) phase instability and microstructural heterogeneity.

Porosity and gas tightness

Incomplete splat filling and rapid solidification inherently result in lamellar and porous microstructures in thermally sprayed coatings, respectively. Although controlled porosity is advantageous for promoting gas diffusion and expanding the active surface area, excessive or improperly connected pores can disrupt percolation pathways and inhibit electrochemical activity. In solid oxide systems, the best performance is obtained at a percolation threshold, with the maximum triple-phase boundary (TPB) density and minimal mechanical integrity. Beyond this regime, increased porosity leads to reduced interfacial contact, coarsening of the active phases, and diminished electrochemical activity [93,94].

Figure 6 shows the method used to measure the active TPBs in the materials. An in-house algorithm developed in MATLAB was used in this study for active TPB quantification of a given 3D matrix, which contains three segmented phases (*i.e*. red: Ni, cyan: YSZ, and blue) [95].

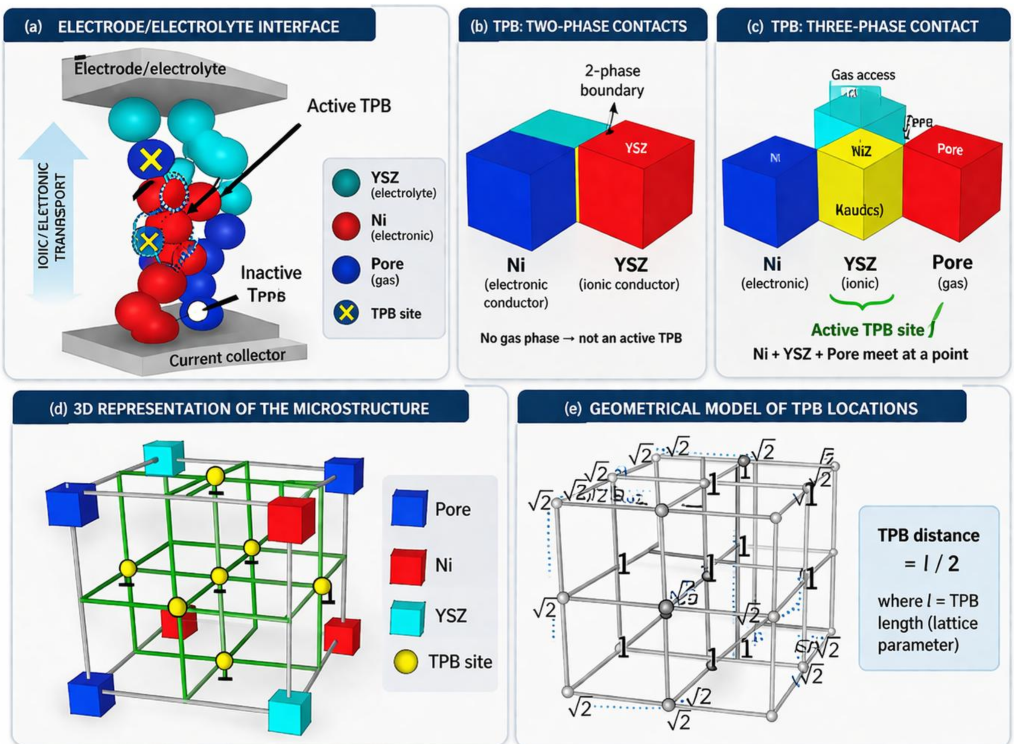

Figure 6. *Active TPBs occur only where the ionic conductor (YSZ), electronic conductor (Ni) and gas phase (pore) meet. The density and connectivity of these defects govern the electrochemical performance [95] (CC BY 4.0 Attribution)*

Interconnected pores serve as routes for electrolyte penetration and gas leakage, accelerating corrosion and parasitic reactions. In battery systems, these effects are reflected in increased electrolyte infiltration, unstable SEI/CEI formation, and uneven current distribution. However, excessively thick coatings can impede ion transport and increase diffusion resistance, particularly when the coating has low ionic conductivity. Hence, the pore size distribution, connectivity, and volume fraction should be highly controlled to avoid compromising the transport efficiency and structural stability in the design of thermal-spray coatings [96].

Figure 7 presents a comprehensive analysis of the gas-barrier characteristics of ceramic tubes coated with lanthanum strontium titanate (LST) and lanthanum strontium manganite (LSM). In Figure 7(a), the images show the same dark coats of LST and LSM on the outer surfaces of the porous ceramic tubes, indicating good formation of gas-sealing layers (GSLs). In Figure 7(b), the leakage rates of the as-sprayed and 1200 °C-annealed coatings are compared. Both the LST and LSM coatings exhibited significant reductions in leakage after high-temperature treatment, but LST showed a lower leakage rate than LSM. Figure 7(c) shows the results of further modifications [97].

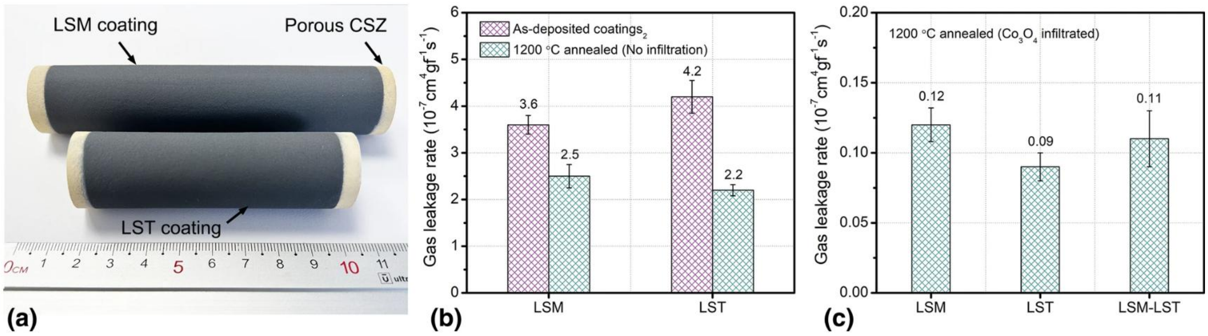

Figure 7. *(a) Images of LST and LSM coatings applied to a porous ceramic tube, (b) the gas leakage rates for both the as-sprayed and 1200 °C-treated LSM and LST coatings, and (c) the gas leakage rates for LST-Co_3O_4 and LSM-Co_3O_4 coatings, as well as the LSM-LST bilayer coating after incorporating Co_3O_4 [97]*

In SOFC applications, LSM tubes are crafted to ensure gas tightness while withstanding high-temperature conditions. Using LSM as a coating material is essential for reducing oxidation rates, which is vital for maintaining gas tightness over time.

Interfacial bonding and mechanical integrity

Interfacial bonding between splats and at the coating-substrate interface is a crucial determinant of coating performance. Inadequate metallurgical bonding and a low effective contact area result from weak inter-splat cohesion due to insufficient particle melting or in-flight oxidation. This increases electrical resistance and leads to mechanically weak interfaces that are prone to delamination under thermal and mechanical loads [98]. The lamellar structure also facilitates crack initiation and propagation along inter-splat boundaries, especially during cyclic thermal or electrochemical deformation. These cracks may form networks with one another, promoting electrolyte ingress and accelerating degradation mechanisms such as corrosion and oxidation. Experimental research has shown that coating deposition results in lower wear rates and reduced mechanical durability compared with its well-bonded counterpart [99]. Figure 8 shows that materials with numerous tiny holes, weak interlayer connections, and uncontrolled parts and coatings cause devices to operate inconsistently. This occurs because the materials are not strong and have different chemical activities.

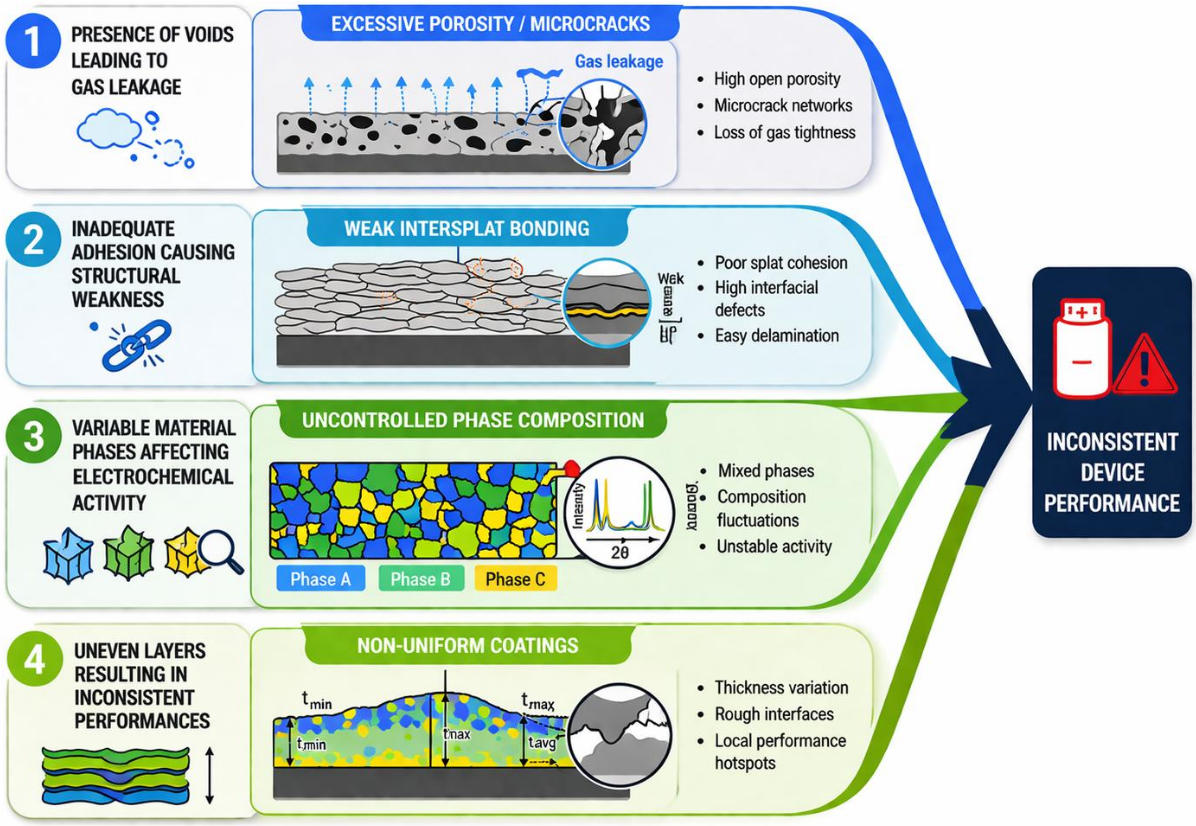

Figure 8. *Microstructural challenges and device performance*

Thermally sprayed coatings have weak interlayers and hence cannot withstand pressure and thermal stress. This causes them to peel and wear off up to 3.5 times faster than finishes with good bond strength. The layered structure is characterized by weak interlayer connections. This contributes to the formation and propagation of cracks in these weak areas under repeated stress. This leaves routes for damage and corrosion to occur. New designs have been inspired by similar issues at the particle scale in Ni-rich lithium-ion battery cathodes. These designs consist of layers with controlled changes in the three-dimensional elements. These gradients modify the positioning of Ni, Co, and Mn to avoid surface alterations, prevent phase jumps, and reduce stress accumulation during the electrochemical cycling. The mechanisms of sticking layers together and of combining materials within particles are both based on the same principle: maintaining surface stability to prevent defect formation [100,101]. $LiNi_xMn_yCo_zO_2$ (NMC) cathodes contain a high Ni content. They can develop small cracks when used repeatedly. These cracks can expose new surfaces to unwanted reactions and separate the active material from the electrode, causing damage and loss of capacity. Many believe that these cracks occur because the particles change shape unevenly during their use. However, recent studies suggest that certain electrolytes may reduce the occurrence of these cracks during deep cycling [102]. High-density energy storage poses several challenges that must be addressed. These challenges affect Li-ion batteries, the market leader, as well as emerging technologies such as Na-ion and Mg-ion batteries. All these methods use similar materials. Therefore, finding solutions is important. These methods help reduce stress and prevent defects [103-105]. The interaction between the surfaces and the chemicals affects the adhesion between the metal and the rubber. This involves the movement of charged particles and chemical reactions to maintain the stability of the coating. In the weaker coatings, the particles moved along the surface. In stronger coatings, they spread more widely. This creates a layer that slows down but does not control the reaction speed [106].

Phase stability and non-equilibrium microstructures

Thermal plasma treatment, particularly RF plasma treatment, can improve the properties of particles fabricated using other methods. This process is currently being developed for large-scale application. The advantages and disadvantages of this method were also examined. Another topic is self-propagating high-temperature synthesis, which depends significantly on the initial formation of the composite particles are first formed [107]. Many electrochemical devices employ ceramic solid electrolytes that conduct a particular ion, but with small amounts of electron leakage. Their degradation mechanisms can be divided into two broad types: a slow transverse mode that builds damage perpendicular to the direction of ionic current flow, and a fast longitudinal mode that builds degradation parallel to the direction of current flow [108]. These parameters affect the deposition efficiency, microstructure, and mechanical properties of the coatings. These settings must be optimized to produce high-quality, uniform coatings [109].

One way to solve these problems is to use special coatings that conduct ions and chemically adapt to the environment. Li^+ can form bonds with bridging-type oxygen in metal oxide materials. The model exhibited a relaxation process during the intercalation. This is easier to observe when transport is fast in both the solid and liquid/electrolyte phases of a small, uniform medium, or when the SOC is high. The rate of the Li-ion intercalation reaction in various small host materials can be predicted from their characteristic frequencies [110,111].

Process scalability and reproducibility

One of the weaknesses of using TSC to cover electrochemical systems is the difficulty of maintaining its quality at scale. This process is highly sensitive to interdependent parameters, including plasma characteristics, feedstock properties, spray distance, and substrate conditions. Even minor differences in parameters can cause major alterations in the microstructure, resulting in variations in coating performance [112].

In the case of advanced battery architectures, especially those using three-dimensional or micro-structural components, it is difficult to achieve uniform coating coverage and thickness. Localized stress concentrations, uneven electrochemical activity, and premature failure can be caused by non-uniform deposition. Additionally, there are no existing studies on integrating TSC processes into current battery manufacturing, creating further difficulties for their industrial applications [113,114]. Future development will require a synergy of the development of new materials, process control, and multiscale characterization to establish a robust process-structure-property relationship [115].

Future directions and emerging trends in thermal spray coatings technology

More attention should be paid to the interface design of TSC technologies for energy systems in the future. This is because low porosity and a high contact area are more desirable for reducing resistance and improving battery life [116]. Table 3 shows how TSC technologies can help extend battery life. It links the materials used, processing challenges, and surface features [106,117-120].

Functionally graded materials (FGMs) are novel materials with composition variations in a specific spatial direction. FGMs offer specific advantages over traditional homogeneous materials when subjected to thermomechanical cyclic loading and when specific protective requirements must be met [121,122].

Research will focus on developing smart monitoring and early-warning systems, including AI and machine learning technologies, to detect emerging thermal-runaway risks. Advances in materials science will open new avenues for thermal runaway prevention and battery safety, especially through nanotechnology and self-healing materials.

***Table 3.** Enhancing battery durability and efficiency through TSC technologies*

Technology	Materials composition	Key challenges	Quantitative metrics	Electrochemical impact	Ref.
APS	Al_2O_3-TiO_2 coated NMC cathode	Oxide formation and microcracking	Porosity: 15 % Adhesion: 35 MPa	Capacity retention improved to 81.8% at 25 °C	[117]
HVOF	Ti porous transport layer (PEM)	Residual stress *vs.* transport	Porosity: 30 % Adhesion: 65 MPa	Enhanced gas diffusion and reduced contact resistance	[106]
Cold spray	Cu current collectors	Residual stress accumulation	Porosity: <5 % Adhesion: 95 MPa	Improved electrical conductivity and mechanical durability	[118]
SPS	YSZ, NiO-YSZ, LSM, LSCF, $MnCo_2O_4$-based coatings	Porosity control, thermal mismatch, phase stability, coating durability	Electrolyte density >95 % Electrode porosity 20-40 % Coating thickness 20-500 µm	Enhanced ionic transport, reduced interfacial resistance, improved corrosion resistance and SOFC efficiency	[119]
FGMs	Ni-YSZ graded interfaces	Thermal mismatch	CTE mismatch reduced by ~30 %	Reduced crack formation and delamination	[120]

The seamless integration of intelligent monitoring and response systems in battery-safe coatings is anticipated to transform battery safety, enabling rapid emergency responses at the early stages of thermal runaway [123-126]. Moving forward, continued research and development of renewable energy storage solutions are needed to further improve their performance and scalability. Studies on the environmental impact of different energy storage systems are important for sustainable energy solutions. New solutions are needed in the fields of energy and hydrogen storage to satisfy the growing energy demand [127]. It will be faster to introduce new resources, implement controlled process management, monitor data, and make data-driven improvements. These trends reflect a trend towards interface-oriented designs. To develop effective and powerful energy systems, porosity, bonding, and structure must be controlled [128].

Artificial intelligence for thermal spray coatings in electrochemical energy storage

The integration of AI into electrochemical energy storage and TSC significantly improves the performance and reliability of these systems by providing advanced data-driven approaches. AI algorithms can be applied to electrochemical energy storage, where they can analyse large amounts of data related to battery performance and thermal energy storage (TES) systems to forecast degradation [129].

In TSC, AI is used to develop machine learning models that optimize coating parameters and forecast coating properties from process parameters. AI can employ optimization algorithms to refine coating composition and deposition parameters, thereby enhancing durability, adhesion, and thermal resistance. Such capabilities accelerate the evolution of high-performance coatings with tailored functionalities by drastically reducing trial and error and allowing adaptive control in the manufacturing process [130-132].

The use of sensors and AI together will help adjust the process in real time. This will make the process more consistent and reduce errors. In addition, digital twin models enable the integration of processing conditions, microstructural modifications, and device electrochemical performance across various scales. With this integration, degradation mechanisms, such as interfacial oxidation and microcracking, can be predicted [133].

Recent advances in artificial intelligence (AI) have significantly contributed to the design of materials for electrochemical energy storage systems (EESS). Data-driven methods and ML assist in rapidly generating new materials. These technologies consider a wide variety of chemical alternatives, enhance material properties, and accelerate the discovery of new materials. This can make energy storage systems more effective in the future. Material-designing AI is also used to modernize outdated systems and produce new energy-storage systems [134]. The use of AI and ML tools assists in the discovery of multidimensional materials, as traditional methods are difficult to execute successfully. These tools not only result in high-throughput discovery but also accelerate most virtual screening and inverse molecular design operations. With feature engineering, alternative sets of material descriptors can be applied to optimize the material design and enhance the performance of EESSs [135]. Simulations that involve multiple physical processes (so-called multi-physics simulations) are challenging and offer opportunities in science and engineering [136].

The multi-scale, multi-physics model shown in Figure 9 was used to predict the behaviour of reactor fuel cladding containing hydrogen in the form of hydride inclusions. To estimate the stress conditions within the fuel cladding at 1200 °C, a macroscale fuel rod model was first used. After being identified in the multiscale integration of the calculation, these conditions were subsequently forwarded to coupled phase-field mesoscale calculations to determine the morphology of the hydride inclusion. This morphology was further scaled for mesoscale calculations to obtain the stress distribution in the cladding [137].

Neural networks can complete certain tasks rapidly and accurately. Simulations that obey the rules of physics are beneficial and require proper management of computers and software. Combining ML with other computing approaches can open new opportunities for simulations but also complicate the process [138-141]. Future studies should focus on maximizing frit formulations to enhance thermal compatibility and adhesion, as well as evaluating the mechanical, thermal, and leaching resistance of the coatings under service conditions. Overall, the results of this study indicate that the TSC battery materials are far more complex than mere surface remelting suggests.

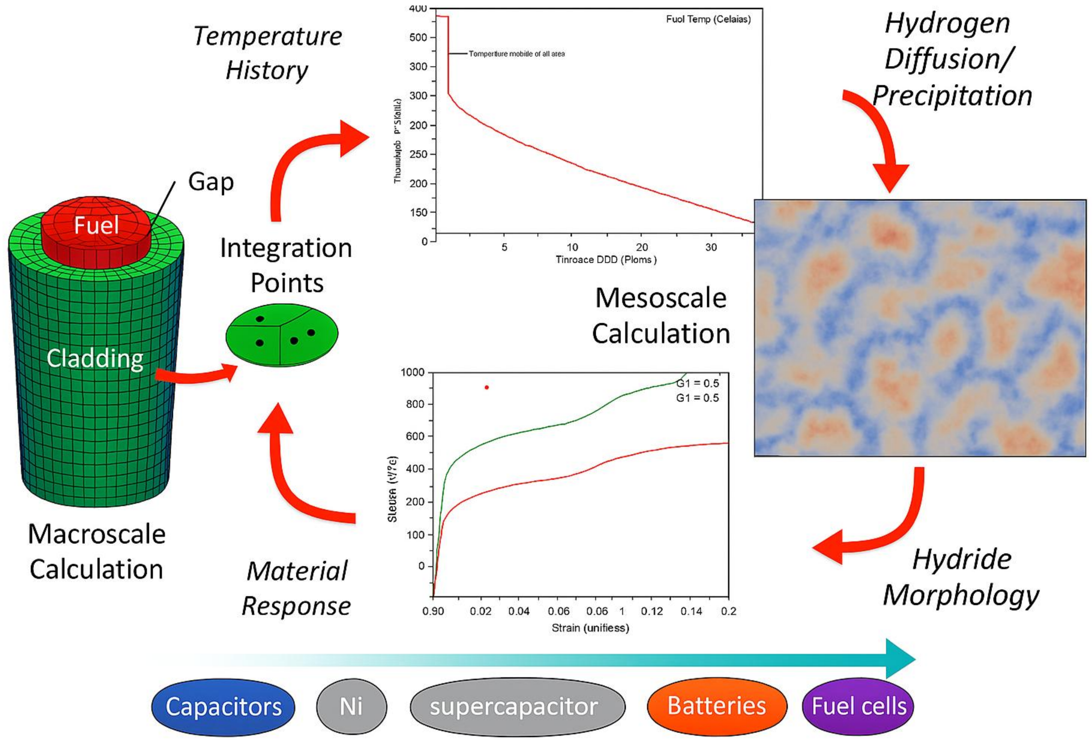

Figure 9. *Multi-scale multi-physics approach for forecasting the behavior of reactor fuel cladding in the presence of hydrogen [137] (CC BY 4.0 Attribution)*

Conclusion

The detailed protocols were discussed, and the best ones proposed are summarized as follows:

- The common problems (interfacial degradation, transport limitations, and mechanical stresses) that can be overcome with the microstructure and compositional gradient of TSC are emphasized. The TSC process (APS, VPS, SPS, HVOF, and cold spray) is scalable and adaptable for various applications and enables the production of coatings with high durability and performance at large scale.

- Thermal spray-generated protective oxide coatings (Al_2O_3, TiO_2, and ZrO_2) help suppress side reactions, dendrite growth, and electrolyte infiltration, which are relevant to cycling stability, and increase Li^+ transport and mechanical strength. TSC facilitates the development of conductive bipolar plates and electrodes with superior porosity and microstructures that are both corrosion-resistant and durable under low-temperature and acidic conditions, thereby optimizing hydrogen production efficiency and longevity.
- High-temperature stable ceramic coatings (YSZ, LSM, and LSCF) produced by suspension plasma spraying and other methods can form a gas-tight, ion-conductive coating layer and have graded interfaces to control thermal expansion and extend the operational life of the product. It was explained that the porosity, splat bonding, and phase distribution of the coating depend on precise control of particle properties, velocity, and temperature; all of these factors affect ionic/electronic transport and mechanical integrity across all three systems. The need to balance porosity for gas diffusion, active surface area, electrical conductivity, and mechanical strength is discussed. Graded and multilayer coatings are highlighted for their ability to reduce thermal mismatch and crack propagation, thereby improving durability in cyclic operating environments.
- Although thermal spray coatings have great potential, there are still many problems to be solved, such as uniform coating deposition on complicated-shaped parts, maintaining the stability of the coating phase under the high-speed solidification condition, and obtaining stable coating quality and performance in large-scale industrial production. The current developments in process control using AI, multiscale modelling, and in situ diagnostics are expected to provide better control of coating quality and identification of degradation paths. This study highlights the need for ongoing research, policy implementation, and industrial uptake of electrochemical energy devices to achieve scalable, low-cost, and resilient energy devices.

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