

# Surface passivation

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*"In space, no one can hear you think."*

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# 1 Surface passivation

## 1.1 Introduction to Surface Passivation

Surface passivation stands as one of the most fundamental yet often invisible processes that shape the performance and longevity of materials across countless technological and natural systems. At its core, passivation represents nature's and humanity's ingenious solution to an inherent problem: the relentless reactivity of surfaces exposed to challenging environments. From the rust-resistant sheen of stainless steel cutlery gleaming on a dining table to the microscopic protective layers enabling modern microprocessors to function reliably, passivation silently underpins much of our material world. This transformative process involves deliberately or naturally inducing a state of "passivity" in a material surface—essentially rendering it less chemically reactive—through the formation of an ultra-thin, adherent surface layer that acts as a barrier against further interaction with the surrounding environment. The distinction between active and passive surfaces forms the conceptual bedrock of this field: active surfaces, like freshly cut iron that rapidly oxidizes in humid air, readily participate in chemical reactions, while passive surfaces, such as the chromium oxide layer on stainless steel, resist such interactions, maintaining their integrity and functionality over extended periods. This transformation hinges on the concept of surface energy, a measure of the excess energy at a material's boundary compared to its bulk. High-energy surfaces, being thermodynamically unstable, tend to react with their environment to achieve lower energy states, often through passivation. For instance, aluminum's high surface energy drives its immediate reaction with atmospheric oxygen to form a protective alumina layer, effectively lowering the system's energy while shielding the underlying metal from further oxidation. The elegance of passivation lies in its ability to create these protective nanoscale barriers—often just nanometers thick—that dramatically alter macroscopic material behavior without significantly changing the material's bulk properties.

The importance of surface passivation in material science cannot be overstated, as it directly addresses the universal challenge of material degradation. Every year, corrosion alone costs global economies an estimated 2.5 trillion USD, equivalent to approximately 3.4% of the world's GDP, according to comprehensive studies by NACE International. This staggering figure encompasses not only direct replacement costs but also indirect losses from maintenance, downtime, and environmental contamination. Passivation serves as a primary defense mechanism against such degradation, extending material lifespans from months to decades in critical applications. Consider the Golden Gate Bridge, whose iconic orange paint is far more than mere decoration—it's a sophisticated passivation system that must be constantly maintained to protect the structural steel from the corrosive salt spray of San Francisco Bay. Similarly, in the biomedical field, titanium implants owe their biocompatibility and longevity to a spontaneously formed titanium oxide passivation layer that prevents metal ion release and adverse biological reactions, allowing hip replacements to function reliably for over fifteen years in most patients. Beyond preventing degradation, passivation enables materials to perform functions that would otherwise be impossible. Silicon, for example, would be useless in electronics without its ability to form a near-perfect silicon dioxide passivation layer, which allows for the precise electrical isolation needed in transistors. The economic implications ripple across industries: properly passivated aerospace components reduce inspection frequency and replacement costs in aircraft, while

passivated pharmaceutical processing equipment prevents contamination that could lead to costly recalls and regulatory penalties. In essence, mastering surface passivation transforms materials from vulnerable entities into resilient performers, unlocking technological possibilities while conserving resources and reducing environmental impact.

The applications of passivation span an extraordinary range of fields, demonstrating its cross-disciplinary nature and universal relevance. In semiconductor manufacturing, passivation is the unsung hero of the digital revolution. The silicon dioxide layers grown on silicon wafers—achieved through thermal oxidation at temperatures exceeding 1000°C—create atomically precise interfaces that enable the billions of transistors in modern microprocessors to function without electrical interference. This process, perfected over decades, allowed Moore’s Law to progress from early integrated circuits with a handful of components to today’s chips with tens of billions of transistors. Equally critical is the passivation of solar cells, where anti-reflection and surface passivation coatings boost photovoltaic efficiency by minimizing electron recombination at surfaces, directly impacting the viability of renewable energy. In the realm of corrosion protection, anodizing transforms aluminum into a corrosion-resistant and aesthetically versatile material by thickening its natural oxide layer through electrochemical processes. This technique protects everything from aircraft fuselages to consumer electronics casings, while chemical passivation treatments for stainless steel—using nitric acid or citric acid baths—ensure medical instruments and food processing equipment remain hygienic and durable. Biomedical applications extend beyond implants to include passivated drug delivery systems, where surface treatments control the release kinetics of therapeutic agents. Energy storage systems rely crucially on passivation: in lithium-ion batteries, the solid-electrolyte interphase (SEI) that forms on graphite anodes during the first charge cycle is a passivation layer that prevents continuous electrolyte decomposition while allowing lithium-ion transport, determining battery cycle life and safety. Even in cultural heritage preservation, scientists apply passivation techniques to protect ancient bronze artifacts from further corrosion, such as the treatment of the Statue of Liberty’s copper skin during its 1980s restoration. These diverse applications share common underlying principles that will be explored throughout this article, revealing how fundamental surface science translates into practical solutions across human endeavors.

To navigate the technical landscape of surface passivation, a foundational vocabulary and conceptual framework must be established. The term “passive layer” refers to the protective film that forms on a material surface, which may be an oxide, nitride, sulfide, or other compound depending on the material and environment. This layer is often distinct from the “native oxide,” which forms spontaneously on many metals upon air exposure, such as the 2-5 nm thick aluminum oxide that appears within microseconds on freshly exposed aluminum. Electrochemically, the “breakdown potential” signifies the critical voltage above which a passive film loses its protective properties, leading to localized corrosion like pitting—a phenomenon vividly demonstrated when stainless steel exposed to chloride ions exceeds its breakdown potential. Beyond this threshold lies the “transpassive region,” where increased current density causes either passive film dissolution or oxygen evolution, depending on the material system. Surface science provides additional essential concepts: “surface free energy” quantifies the thermodynamic driving force for surface reactions, with high-energy surfaces being more prone to passivation. “Adsorption” describes the accumulation of atoms or molecules at surfaces, which often initiates passivation, such as when oxygen adsorbs on titanium before

oxide formation. “Surface states” refer to electronic energy levels at surfaces that differ from the bulk, critically affecting semiconductor passivation where these states can trap charge carriers and degrade device performance. The interplay of these concepts explains why passivation processes can be both spontaneous and engineered, natural and technologically refined. For instance, the passive layer on iron in concentrated nitric acid—first systematically studied by Christian Friedrich Schönbein in the 1830s—forms naturally under specific conditions, while the silicon dioxide layers in integrated circuits result from precisely controlled thermal processes. Understanding this terminology and conceptual framework provides the necessary tools to appreciate the historical development, fundamental principles, and advanced applications of surface passivation that will unfold in subsequent sections of this comprehensive exploration.

The journey through surface passivation will next delve into its historical evolution, tracing humanity’s growing understanding from ancient metallurgical practices to cutting-edge nanotechnology. Early civilizations unknowingly harnessed passivation when they observed that certain copper alloys developed protective patinas, while Renaissance metalworkers noted that mercury-treated gold surfaces resisted tarnishing. These empirical observations gradually gave way to systematic scientific inquiry in the late 18th and 19th centuries, when researchers like James Keir and Michael Faraday began to unravel the electrochemical mysteries underlying passivation phenomena. The historical narrative reveals how industrial demands—from protecting naval ships to manufacturing reliable electronics—drove innovations in passivation techniques, ultimately leading to the sophisticated processes that underpin modern technology. This historical context not only illuminates the scientific milestones but also highlights the enduring interplay between fundamental research and practical application that continues to advance the field today.

## 1.2 Historical Development of Passivation

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2.2 Scientific Understanding in the 19th and Early 20th Century - Michael Faraday’s electrochemical studies in the 1830s - Development of oxide film theory by Ulick R. Evans and others - Evolution from simple chemical explanations to sophisticated electrochemical models

2.3 Industrial Revolution and Passivation - Industrial needs driving passivation development in the 19th and early 20th centuries - Early industrial applications - Relationship between industrial growth and standardized passivation processes

2.4 Modern Era of Passivation Research - Post-WWII developments, especially in semiconductor industry - Impact of new analytical tools on research - Key research breakthroughs in late 20th century

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### 1.3 Section 2: Historical Development of Passivation

The historical narrative of surface passivation reveals a fascinating journey from empirical observations to sophisticated scientific understanding, paralleling humanity's broader quest to master materials and their interactions with the environment. This journey begins not in laboratories, but in the workshops and foundries of ancient civilizations, where artisans and metalworkers, though lacking scientific terminology, intuitively recognized and exploited passivation phenomena through centuries of trial and error. The remarkable durability of ancient bronze artifacts, some surviving millennia with minimal degradation, stands as testament to early unwitting mastery of passivation. The Statue of Marcus Aurelius in Rome, remarkably preserved for nearly two millennia while other bronze statues were melted for their metal value, owes its survival partly to the formation of a stable protective patina—a natural passivation layer that shields the underlying bronze from further corrosion. Similarly, ancient metallurgists in India developed the famous Delhi Iron Pillar in the 4th century AD, which has resisted corrosion for over 1,600 years in Delhi's humid climate, due to an unexpectedly high phosphorus content that contributed to the formation of a protective passive film. These ancient achievements, while not understood in modern scientific terms, demonstrate an empirical grasp of surface chemistry that would only be systematically explored millennia later.

The first documented scientific observation of passivation emerged in the late 18th century, marking the transition from empirical practice to systematic inquiry. In 1790, Scottish chemist and industrialist James Keir recorded his meticulous observations that iron, when immersed in concentrated nitric acid, initially reacted vigorously but then suddenly became inert, resisting further reaction even when transferred to other acids like sulfuric acid that would normally attack it vigorously. This remarkable phenomenon, which Keir described in a letter to James Watt, represented one of the first scientific descriptions of passivation. Keir's keen observation revealed that the iron had somehow transformed from an active to a passive state, a concept that would prove revolutionary in understanding surface chemistry. His discovery was particularly noteworthy because it demonstrated that passivation was not merely a property of certain materials but could be induced under specific conditions. The industrialist's scientific curiosity led him to experiment further, finding that this passive state could be disrupted by mechanical disturbance such as scratching the surface, after which the iron would return to its reactive state. This mechanical reactivation phenomenon provided an important clue that passivation involved some form of surface layer that could be physically disrupted.

The systematic study of passivation truly began in the 1830s with the pioneering work of Christian Friedrich Schönbein, a Swiss-German chemist who coined the term "passivity" to describe the phenomenon. Schönbein, already renowned for his discovery of ozone, conducted extensive experiments on iron and steel, metic-

ulously documenting their behavior in various acid environments. His research demonstrated that iron could exist in two distinct states: an “active” state where it readily dissolved in acids, and a “passive” state where it resisted dissolution. Crucially, Schönbein discovered methods of inducing both states: iron could be made passive by treatment with concentrated nitric acid or by anodic polarization (applying a positive electrical potential), while mechanical disturbance or cathodic polarization (negative potential) could restore its active state. This dual approach—chemical and electrochemical—laid the groundwork for understanding that passivation involves surface modification rather than bulk property changes. Schönbein’s work was distinguished by its systematic nature; he carefully controlled experimental conditions and documented the effects of variables such as acid concentration, temperature, and the presence of other substances. His observations that certain substances like chloride ions could □ □ (destroy) passivity while others like chromates could enhance it revealed the complex interplay between environmental factors and surface reactivity. Schönbein’s contributions extended beyond laboratory research; he recognized the practical implications of his findings, suggesting that passive iron might be useful for containers and instruments where corrosion resistance was essential. In essence, Schönbein transformed passivation from a curious anomaly into a recognized scientific phenomenon worthy of systematic study, establishing the foundation for all subsequent research in the field.

The middle decades of the 19th century witnessed a quantum leap in understanding passivation, largely through the brilliant work of Michael Faraday, whose electrochemical investigations provided the theoretical framework that continues to underpin modern passivation science. Faraday, already celebrated for his fundamental contributions to electromagnetism and electrochemistry, turned his attention to iron passivity in the 1830s, conducting a series of elegant experiments that revealed the electrochemical nature of the phenomenon. His approach was characteristically thorough: he demonstrated that iron could be passivated not only by chemical treatment with nitric acid but also by making it the anode in an electrochemical cell, confirming Schönbein’s observations about anodic polarization. Faraday’s crucial insight was recognizing that passivation involved the formation of an extremely thin surface film that altered the electrochemical behavior of the iron. He proposed that this film, though invisible to the naked eye, acted as a barrier between the reactive metal and its environment. This was a revolutionary concept at the time, suggesting that surfaces could possess properties dramatically different from the bulk material. Faraday’s experiments with different metals revealed that passivation was not unique to iron; he observed similar phenomena with nickel, cobalt, chromium, and aluminum, each forming protective films under appropriate conditions. His work introduced the important distinction between spontaneous passivation (occurring naturally in certain environments) and induced passivation (requiring specific treatment). Perhaps most significantly, Faraday established that passivation was an electrochemical process governed by the principles of oxidation and reduction, laying the groundwork for the modern electrochemical understanding of corrosion and passivation. His experimental techniques, including the careful measurement of electrical currents and potentials during passivation and reactivation, set new standards for scientific rigor in surface chemistry research.

Following Faraday’s foundational work, the late 19th and early 20th centuries saw the gradual development of competing theories attempting to explain the nature of passive films, reflecting the broader scientific debate about the fundamental nature of matter and energy during this period. Two principal theories emerged: the oxide film theory and the adsorption theory. The oxide film theory, which eventually gained broader ac-

ceptance, proposed that passivation resulted from the formation of a thin, continuous oxide layer on the metal surface, physically separating it from the corrosive environment. This theory was championed by researchers like Robert Wilhelm Bunsen, who demonstrated that the thickness of passive films could be measured using optical interference techniques, providing some of the first quantitative evidence for the existence of these ultrathin layers. Bunsen's measurements revealed that passive films were extraordinarily thin—on the order of nanometers—explaining why they were often invisible yet still effective barriers. The competing adsorption theory, advanced by scientists including Frederick Guthrie, suggested instead that passivation resulted from the adsorption of oxygen or other species onto the metal surface, forming a monolayer that altered the surface energy without necessarily forming a distinct oxide phase. This debate persisted for decades, partly because the analytical tools available at the time were insufficient to definitively resolve the nature of passive films. It wasn't until the development of more sophisticated analytical techniques in the mid-20th century that the oxide film theory gained conclusive support for most metal systems, though adsorption processes were recognized as important initiation steps in passivation.

The early 20th century witnessed significant refinements in passivation theory, particularly through the work of Ulick Richardson Evans, a British corrosion scientist who made substantial contributions to understanding the electrochemical mechanisms of passivation. Evans, often regarded as the father of modern corrosion science, conducted extensive research in the 1920s and 1930s that helped establish the oxide film theory on a more rigorous scientific footing. His experiments demonstrated that passive films were not static but dynamic structures, constantly reforming when damaged and existing in a state of equilibrium with the surrounding environment. Evans introduced the concept of the “critical current density”—the minimum anodic current required to initiate passivation—and showed how this parameter varied with different metals and environmental conditions. His work also revealed the importance of film composition; for instance, chromium in stainless steel formed a particularly stable passive film of chromium oxide, explaining the superior corrosion resistance of these alloys compared to plain carbon steel. Evans's research extended beyond fundamental science to practical applications; he developed methods for testing passivation efficiency and established standards for evaluating corrosion resistance that would later be adopted by industry. His comprehensive book “Corrosion and Oxidation of Metals,” published in 1960, synthesized decades of research and became a definitive reference in the field. Importantly, Evans recognized the limitations of purely chemical explanations for passivation and helped develop more sophisticated electrochemical models that could account for the complex interplay of factors influencing passivation, including potential, pH, temperature, and the presence of aggressive ions like chlorides.

The Industrial Revolution of the 19th century created unprecedented demand for materials that could withstand harsh operating environments, driving practical developments in passivation technology even as scientific understanding was still evolving. The expansion of railroads, for example, required better protection for iron rails, bridges, and rolling stock exposed to weather and mechanical stress. Early railway engineers discovered that certain treatments, such as painting with linseed oil or applying tar-based coatings, could significantly extend the service life of iron components—crude forms of passivation that created barrier layers between the metal and its environment. The chemical industry, burgeoning during this period, faced particularly acute challenges with corrosion-resistant equipment. Sulfuric acid production, central to many



industrial processes, required containers that could withstand highly corrosive conditions. The serendipitous discovery that lead formed a protective lead sulfate layer in sulfuric acid environments made it the material of choice for acid chambers and piping—an early example of natural passivation being exploited industrially. Similarly, the development of the lead-chamber process for sulfuric acid production relied on the passivation of lead by the reaction products, enabling the construction of large-scale acid plants that would have been impossible with unpassivated materials. These industrial applications preceded scientific understanding; engineers utilized passivation phenomena effectively through empirical observation and trial-and-error, even without knowing the underlying mechanisms.

The late 19th and early 20th centuries witnessed the emergence of more systematic industrial approaches to passivation, particularly in the burgeoning fields of electrical engineering and transportation. The telegraph industry, for example, required reliable underground and underwater cables that could resist corrosion for decades. Early cable manufacturers discovered that copper conductors could be protected by various treatments, including alloying with small amounts of arsenic or antimony, which promoted the formation of more stable passive films. The development of the transatlantic telegraph cable in the 1860s represented a triumph of empirical passivation technology, with copper conductors protected by layers of gutta-percha and other materials that prevented seawater corrosion. Similarly, the rapidly expanding electrical power industry faced challenges with corrosion in generators, transformers, and transmission infrastructure. Engineers discovered that certain metals and alloys, particularly copper and aluminum, formed protective oxide layers that prevented further degradation in electrical applications. Aluminum, despite its high reactivity, proved invaluable for electrical transmission lines precisely because of its ability to form a thin, adherent, and electrically insulating oxide layer that protected the underlying metal while minimally affecting conductivity. The automotive industry, emerging in the early 20th century, created new demands for corrosion-resistant materials. Early automobile manufacturers experimented with various metal treatments, including phosphating and chromating processes that formed conversion coatings on steel surfaces—essentially engineered passive films that improved paint adhesion and corrosion resistance. These industrial developments occurred somewhat independently of academic research, with practical solutions often preceding theoretical understanding.

The relationship between industrial growth and standardized passivation processes became particularly evident during World War I and the interwar period, when military demands accelerated technological innovation in materials science. The need for reliable naval vessels, for example, drove research into more effective methods of protecting steel hulls from seawater corrosion. The British Royal Navy conducted extensive studies on cathodic protection and sacrificial anodes—techniques that work in conjunction with natural passivation to extend the service life of ships. The development of stainless steel during this period represented a landmark achievement in industrial passivation. Harry Brearley's discovery in 1913 that adding chromium to steel produced a material highly resistant to corrosion was based on empirical observation, but subsequent research revealed that chromium's effectiveness stemmed from its ability to form a stable, self-repairing chromium oxide passive film. This discovery transformed numerous industries, from cutlery manufacturing to chemical processing equipment. During the 1920s and 1930s, standardized passivation processes began to emerge, particularly for stainless steel. The American Society for Testing and Materials (ASTM) established some of the first formal standards for passivation treatments, such as immersion in nitric acid

solutions to remove free iron particles from stainless steel surfaces and enhance the formation of protective chromium oxide films. These standards reflected growing industrial recognition that consistent, controlled passivation procedures were essential for reliable performance in critical applications. The chemical processing industry, expanding rapidly during this period, developed more sophisticated passivation treatments for equipment handling corrosive substances. Nickel-based alloys like Monel, consisting primarily of nickel and copper, found extensive use in chemical plants due to their ability to form protective passive films in various corrosive environments. The standardization of passivation processes during this period marked an important transition from empirical, craft-based approaches to more systematic, scientifically informed industrial practices.

The post-World War II era ushered in a revolution in passivation research, driven largely by the emerging semiconductor industry and enabled by unprecedented advances in analytical instrumentation. The invention of the transistor in 1947 by Bell Laboratories researchers John Bardeen, Walter Brattain, and William Shockley created an immediate need for ultra-pure silicon with perfectly controlled surface properties. While silicon had been known to form a protective oxide layer since the 19th century, the requirements for semiconductor applications were orders of magnitude more stringent than any previous application. Early semiconductor researchers discovered that the electrical properties of silicon devices were extremely sensitive to surface conditions, with unpassivated surfaces exhibiting high densities of electronic states that trapped charge carriers and degraded device performance. This realization catalyzed intensive research into silicon passivation, culminating in the development of thermal oxidation processes that could produce near-perfect silicon dioxide layers on silicon surfaces. The breakthrough came in the late 1950s when Mohamed Atalla and Dawon Kahng at Bell Laboratories discovered that thermally grown silicon dioxide could effectively passivate silicon surfaces, reducing surface state densities by several orders of magnitude and enabling the reliable operation of metal-oxide-semiconductor (MOS) devices. This discovery was foundational to the development of integrated circuits and ultimately the entire digital revolution. The perfection of silicon passivation technology allowed Gordon Moore's famous prediction—later known as Moore's Law—to be realized, as the ability to create increasingly complex integrated circuits depended critically on maintaining precise control over surface properties through passivation.

The explosive growth of the semiconductor industry in the 1960s and 1970s drove parallel advances in analytical techniques for studying passivation layers, creating a virtuous cycle of technological innovation and scientific understanding. Transmission electron microscopy (TEM), developed in the 1930s but refined in the post-war period, allowed researchers to directly image passive films at near-atomic resolution for the first time. These images revealed the remarkable uniformity and structural perfection of thermally grown silicon dioxide layers, explaining their effectiveness as passivation films. X-ray photoelectron spectroscopy (XPS), developed in the 1950s by Kai Siegbahn, enabled chemical analysis of the outermost atomic layers of materials, providing unprecedented insight into the composition and bonding in passive films. XPS studies confirmed that the chromium oxide passive film on stainless steel was enriched in chromium compared to the bulk alloy, resolving longstanding questions about the mechanism of stainless steel's corrosion resistance. Auger electron spectroscopy (AES), developed in the 1960s, allowed for depth profiling of passive films, revealing gradients in composition from the surface to the bulk material. These analytical techniques,

combined with increasingly sophisticated electrochemical methods like potentiodynamic polarization and electrochemical impedance spectroscopy, transformed passivation from a largely empirical field to a quantitative science. Researchers could now measure film thicknesses with angstrom-level precision, determine chemical compositions of monolayer-thick films, and correlate these structural and chemical features with electrochemical behavior. This newfound analytical power led to the discovery that many passive films were not simple homogeneous oxides but complex structures with multiple layers, incorporating elements from both the substrate and the environment. For instance, the passive film on aluminum was found to consist of a thin inner barrier layer of amorphous aluminum oxide and a thicker outer hydrated layer, with the relative proportions depending on formation conditions.

The late 20th century witnessed numerous key research breakthroughs that expanded the frontiers of passivation science and technology beyond traditional metal systems. In the field of electrochemistry, the work of Marcos Fontana and Norbert Sato in the 1970s and 1980s significantly advanced the understanding of passivation mechanisms, particularly the role of point defects in passive films and the kinetics of film growth and breakdown. Their research provided a more complete theoretical framework for explaining phenomena like localized corrosion and the critical factors affecting passive film stability. In the semiconductor industry, the relentless drive toward smaller device features demanded increasingly sophisticated passivation techniques. The development of chemical vapor deposition (CVD) and plasma-enhanced chemical vapor deposition (PECVD) processes allowed for the deposition of high-quality passivation films at lower temperatures, enabling the fabrication of complex integrated circuits with multiple layers of interconnects. Silicon nitride emerged as an important complementary passivation material to

## 1.4 Fundamental Principles of Passivation

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3.2 Thermodynamics of Surface Reactions - Explain Gibbs free energy in surface reactions - Discuss equilibrium and non-equilibrium surface states - Cover the role of activation energy in passivation

3.3 Kinetics of Passivation - Detail the time-dependent aspects of passivation - Discuss nucleation and growth mechanisms - Explain factors affecting passivation rate

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## **1.5 Section 3: Fundamental Principles of Passivation**

The remarkable journey of passivation from empirical observation to sophisticated technology naturally leads us to examine the fundamental scientific principles that govern these phenomena. While the historical narrative reveals how humanity gradually uncovered passivation's practical applications, the underlying science remained for centuries shrouded in mystery. It was only through the systematic development of electrochemical theory, thermodynamic principles, and kinetic models that researchers could finally explain why certain materials spontaneously form protective layers while others corrode uncontrollably. This theoretical framework not only explains the historical observations of Keir, Schönbein, and Faraday but also provides the foundation for modern passivation technologies that enable everything from microelectronics to corrosion-resistant infrastructure. The fundamental principles of passivation bridge the gap between microscopic surface processes and macroscopic material behavior, revealing how nanometer-thin films can dramatically alter the performance and longevity of materials across diverse applications. Understanding these principles is essential not only for advancing passivation technology but also for predicting material behavior in complex environments and developing new materials with tailored surface properties. As we delve into these scientific foundations, we discover that passivation is governed by elegant physical laws that manifest in remarkably consistent ways across vastly different material systems, from metals to semiconductors to polymers.

### **1.5.1 3.1 Electrochemical Basis of Passivation**

At its core, passivation is fundamentally an electrochemical phenomenon, involving the transfer of electrons and ions between a material surface and its environment. This electrochemical nature explains why passivation can be induced not only by chemical treatment but also by electrical polarization, as Faraday first demonstrated in the 19th century. To understand passivation electrochemically, we must first recognize that most materials in contact with electrolytes undergo simultaneous oxidation and reduction reactions. When a metal like iron is exposed to an aqueous environment, it tends to oxidize (lose electrons) at anodic sites on its surface, while a reduction reaction (gain of electrons) occurs at cathodic sites. In acidic environments, the cathodic reaction typically involves hydrogen evolution, while in neutral or alkaline environments, oxygen reduction predominates. These coupled reactions create an electrochemical cell, with the metal serving as both anode and cathode, driving the corrosion process. Passivation occurs when conditions shift to favor the formation of a protective surface film that inhibits these electrochemical reactions, effectively decoupling the anodic and cathodic processes and dramatically reducing the corrosion rate.

The anodic behavior of materials as a function of applied potential reveals the distinctive electrochemical signature of passivation. When we gradually increase the potential of an electrode (making it more anodic) in a corrosive environment while measuring the resulting current, we observe a characteristic curve that includes active, passive, and transpassive regions. In the active region, at relatively low potentials, the current density increases exponentially with potential, following the Tafel equation that describes electrochemical reaction kinetics. This represents the normal corrosion behavior where the metal dissolves actively. However, as the potential continues to increase, the current may suddenly decrease by several orders of magnitude, marking the transition to the passive region. This dramatic decrease in current signifies the formation of a protective passive film that severely restricts both anodic dissolution and cathodic reduction reactions. Within the passive region, the current density remains relatively low and nearly constant over a wide range of potentials, indicating that the passive film is stable and protective. The current in this region, known as the passive current density, represents the slow, steady-state dissolution or film growth that occurs even under passivating conditions. Eventually, at sufficiently high potentials, the current may begin to increase again, marking either the breakdown of passivation (leading to localized corrosion like pitting) or the onset of transpassive behavior, where the passive film itself begins to dissolve or oxidize to a higher valence state.

The Pourbaix diagram, developed by Marcel Pourbaix in the 1930s, provides a powerful framework for understanding passivation from a thermodynamic perspective. These diagrams map the stable phases of a material in aqueous environments as a function of both potential (on the vertical axis) and pH (on the horizontal axis), creating a kind of “phase diagram” for electrochemical systems. A Pourbaix diagram for iron, for example, shows regions of immunity (where the metal is thermodynamically stable and won’t corrode), corrosion (where the metal will dissolve), and passivation (where a protective oxide or hydroxide layer forms). The boundaries between these regions represent equilibrium conditions, calculated from thermodynamic data. Pourbaix diagrams are invaluable for predicting when passivation might occur spontaneously in a given environment and for designing protection strategies. For instance, the diagram for aluminum shows a large region of passivation covering nearly all pH values and a wide range of potentials, explaining why aluminum forms a protective oxide film in most environments and exhibits excellent corrosion resistance despite its highly negative standard electrode potential. In contrast, the Pourbaix diagram for iron shows a much more limited passivation region, primarily in alkaline and slightly acidic conditions at moderate potentials, explaining why iron is prone to corrosion in many environments unless alloyed with passivating elements like chromium.

The mixed potential theory, developed by Carl Wagner and Walter Traud in 1938, provides a crucial framework for understanding how the anodic and cathodic reactions interact to determine whether passivation occurs spontaneously in a given system. According to this theory, when a metal is immersed in a corrosive environment, it will adopt a potential where the rate of the anodic reaction (metal dissolution) equals the rate of the cathodic reaction (such as oxygen reduction or hydrogen evolution). This potential, known as the corrosion potential or mixed potential, determines the steady-state behavior of the system. Whether passivation occurs depends on the relationship between this mixed potential and the critical potentials for passivation. If the mixed potential falls within the passive region, the material will spontaneously passivate. If it falls in the active region, the material will corrode actively. This explains why the same material can behave very

differently in different environments. For example, stainless steel exhibits excellent corrosion resistance in aerated solutions (where the oxygen reduction reaction shifts the mixed potential into the passive region) but may corrode actively in deaerated acid solutions (where the mixed potential remains in the active region). The mixed potential theory also explains how inhibitors work—by suppressing either the anodic or cathodic reaction, they shift the mixed potential into the passive region, inducing passivation.

The specific electrochemical reactions involved in passivation vary depending on the material and environment but generally involve the oxidation of the substrate material to form a protective compound. For metals and alloys, this typically means oxidation to form oxides, hydroxides, or other inorganic compounds. In the case of stainless steel, for example, the key reaction is the oxidation of chromium:



This reaction forms a protective chromium oxide film that is highly stable and adherent, effectively blocking further reaction between the underlying alloy and the environment. The chromium oxide film is typically only 2-5 nanometers thick but provides excellent protection because it is continuous, non-porous, and has very low electronic and ionic conductivity. For aluminum, the passivation reaction involves:

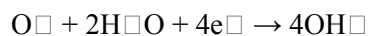


forming an aluminum oxide film that is similarly protective. In semiconductor systems like silicon, the passivation reaction is:



forming silicon dioxide, which is an excellent electrical insulator and provides superb surface passivation for electronic devices. These reactions are all oxidation processes that involve the loss of electrons from the substrate material, coupled with the reduction of some species in the environment (typically oxygen or hydrogen ions).

The cathodic reactions that accompany passivation are equally important, as they provide the electrochemical driving force for the process. In neutral or alkaline environments, the primary cathodic reaction is often oxygen reduction:



This reaction consumes electrons generated by the anodic oxidation of the substrate, driving the overall electrochemical process. In acidic environments, hydrogen evolution may be the dominant cathodic reaction:



The relative rates of these cathodic reactions, compared to the rates of the anodic reactions, determine whether the mixed potential falls in the active or passive region. This explains why aeration (increasing oxygen availability) often promotes passivation of metals like stainless steel by shifting the mixed potential into the passive region, while deaeration (removing oxygen) can cause depassivation and active corrosion.

The breakdown of passivation, leading to localized corrosion, is also fundamentally electrochemical in nature. When the local environment at certain sites on a passivated surface becomes sufficiently aggressive,



the passive film may break down, leading to rapid localized dissolution. This typically occurs when the potential exceeds the breakdown potential (also called the pitting potential) or when the local chemistry becomes unfavorable for passivation. For example, in the case of stainless steel, chloride ions can adsorb to the passive film and locally disrupt it, creating small pits where the metal dissolves actively while the surrounding surface remains passive. The electrochemistry within these pits becomes highly autocatalytic: the hydrolysis of dissolved metal ions produces  $H^+$  ions, lowering the pH and making the environment more corrosive, while the accumulation of positive charge attracts more aggressive anions like chlorides. This creates a self-sustaining localized corrosion cell that can cause significant damage even while the majority of the surface remains passive.

### 1.5.2 3.2 Thermodynamics of Surface Reactions

The electrochemical processes underlying passivation are fundamentally governed by thermodynamic principles that determine the spontaneity and direction of surface reactions. At the heart of these principles is the concept of Gibbs free energy, a thermodynamic potential that combines enthalpy and entropy to predict whether a process will occur spontaneously. For any surface reaction, the change in Gibbs free energy ( $\Delta G$ ) determines its thermodynamic feasibility: if  $\Delta G$  is negative, the reaction is thermodynamically favorable and will proceed spontaneously; if  $\Delta G$  is positive, the reaction is thermodynamically unfavorable and will not occur without an external driving force. In the context of passivation, the formation of a protective surface layer must be thermodynamically favorable for the process to occur spontaneously. For example, the reaction of aluminum with oxygen to form aluminum oxide has a highly negative  $\Delta G$  (approximately -1582 kJ/mol at standard conditions), explaining why aluminum spontaneously forms a protective oxide layer upon exposure to air. Similarly, the oxidation of silicon to form silicon dioxide has a  $\Delta G$  of approximately -856 kJ/mol, making this process highly favorable and explaining the excellent passivation properties of silicon in oxygen-containing environments.

The relationship between Gibbs free energy and electrochemical potential is particularly important for understanding passivation. The standard Gibbs free energy change for a reaction ( $\Delta G^\circ$ ) is related to the standard electrode potential ( $E^\circ$ ) through the equation:

$$\Delta G^\circ = -nFE^\circ$$

where  $n$  is the number of electrons transferred and  $F$  is the Faraday constant (96,485 C/mol). This relationship shows that reactions with highly negative standard free energy changes correspond to highly positive standard electrode potentials, meaning they are strongly thermodynamically favored. For passivation reactions, this thermodynamic driving force must be sufficient to overcome the energy barriers associated with nucleation and growth of the passive film. The actual Gibbs free energy change for a reaction under non-standard conditions is given by:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where  $R$  is the gas constant,  $T$  is the absolute temperature, and  $Q$  is the reaction quotient. This equation shows that the actual driving force for passivation depends not only on the inherent thermodynamics of the

reaction but also on the concentrations of reactants and products. For example, the formation of a passive oxide film is generally favored at higher oxygen concentrations, as reflected in the reaction quotient  $Q$ . This explains why many materials passivate more readily in aerated solutions compared to deaerated ones.

Surface energy plays a crucial role in the thermodynamics of passivation, as it represents the excess free energy associated with atoms at the surface compared to those in the bulk of a material. Atoms at the surface have fewer bonds and are in a higher energy state than atoms in the bulk, creating a thermodynamic driving force for processes that reduce surface energy. Passivation is an effective mechanism for reducing surface energy by forming a stable, low-energy surface layer. For example, a freshly prepared metal surface has a high surface energy due to the presence of unsatisfied bonds, making it highly reactive. When this surface reacts with oxygen to form an oxide, the surface energy decreases significantly because the oxide layer satisfies these unsatisfied bonds, creating a more thermodynamically stable configuration. The reduction in surface energy provides the thermodynamic driving force for spontaneous passivation in many systems.

The concept of equilibrium and non-equilibrium states is essential for understanding passivation phenomena. Many passive films represent metastable states that are not at thermodynamic equilibrium with the environment but are kinetically stabilized by slow reaction rates. For example, the passive film on stainless steel is thermodynamically unstable relative to complete oxidation to rust, but the extremely slow rate of further oxidation allows the film to persist indefinitely under appropriate conditions. This kinetic stabilization is what makes passivation practically useful for corrosion protection. The Pourbaix diagrams mentioned earlier represent thermodynamic equilibrium conditions, but real-world passivation often occurs under non-equilibrium conditions where kinetic factors dominate. The distinction between thermodynamic stability and kinetic stability is crucial: a thermodynamically unstable system can persist indefinitely if the activation energy barriers for transformation are sufficiently high.

The role of activation energy in passivation cannot be overstated, as it determines the kinetics of passive film formation and breakdown. Even when a passivation reaction is thermodynamically favorable ( $\Delta G < 0$ ), it will only proceed at a significant rate if the activation energy barrier is not too high. The activation energy represents the energy barrier that must be overcome for reactants to transform into products, and it is related to the transition state theory of chemical reactions. For passivation processes, the activation energy typically includes contributions from several steps: adsorption of reactants at the surface, nucleation of the passive film, growth of the film, and ionic transport through the film. Each of these steps has its own activation energy, and the slowest step (rate-determining step) governs the overall kinetics of passivation. For example, the formation of aluminum oxide on aluminum has a relatively low activation energy, allowing the reaction to proceed rapidly at room temperature. In contrast, the formation of silicon dioxide on silicon requires higher temperatures (typically above 700°C) to achieve reasonable reaction rates, reflecting a higher activation energy barrier.

The concept of metastability is particularly important for understanding passive films. Many passive films exist in metastable states that are local minima in the free energy landscape, separated from more stable states by activation energy barriers. For example, the amorphous oxide films that form on many metals are metastable relative to crystalline oxides but persist because the activation energy for crystallization is high.



This metastability is often beneficial for passivation, as amorphous films typically provide better protection than crystalline ones due to their lack of grain boundaries and other defects that could serve as fast diffusion paths for corrosive species. The height of the activation energy barriers determines the lifetime of these metastable states: higher barriers lead to longer lifetimes and more stable passivation. This explains why certain passive films, like those on stainless steel or titanium, can provide protection for decades, while others may break down more rapidly under aggressive conditions.

The thermodynamic stability of passive films depends on both the standard free energy of formation of the film material and the interfacial energies between the film, substrate, and environment. The overall thermodynamics of passivation can be analyzed by considering the total free energy change for the system, which includes contributions from the formation of the passive film itself and the creation of new interfaces. For a passive film to be thermodynamically stable, the energy released by forming the film must exceed the energy required to create the new interfaces. This explains why very thin films are often more favorable than thick ones: the energy released by film formation may be insufficient to overcome the interfacial energy requirements for thick films. The critical thickness for thermodynamic stability depends on the specific material system and can be estimated using thermodynamic models. For example, aluminum oxide films are thermodynamically stable up to thicknesses of several nanometers at room temperature, explaining why the natural oxide on aluminum is typically 2-5 nm thick.

The effect of environmental conditions on the thermodynamics of passivation is significant and must be considered for practical applications. Temperature, pressure, and the concentrations of various species in the environment all affect the Gibbs free energy of passivation reactions. Increasing temperature generally increases the rate of passivation reactions (as described by the Arrhenius equation) but may also decrease the thermodynamic stability of certain passive films. For example, some passive films that are stable at room temperature may dissolve or transform at elevated temperatures. The pH of the environment is particularly important for oxide passive films, as it affects the solubility of oxides and hydroxides through acid-base reactions. Many passive films are most stable in neutral to slightly alkaline conditions and become less stable in strongly acidic or alkaline environments. This is reflected in the Pourbaix diagrams, which show how the stability regions of passive films change with pH. The presence of complexing agents or aggressive ions can also dramatically affect the thermodynamics of passivation by forming soluble complexes with components of the passive film, effectively increasing their solubility and destabilizing the film.

### 1.5.3 3.3 Kinetics of Passivation

While