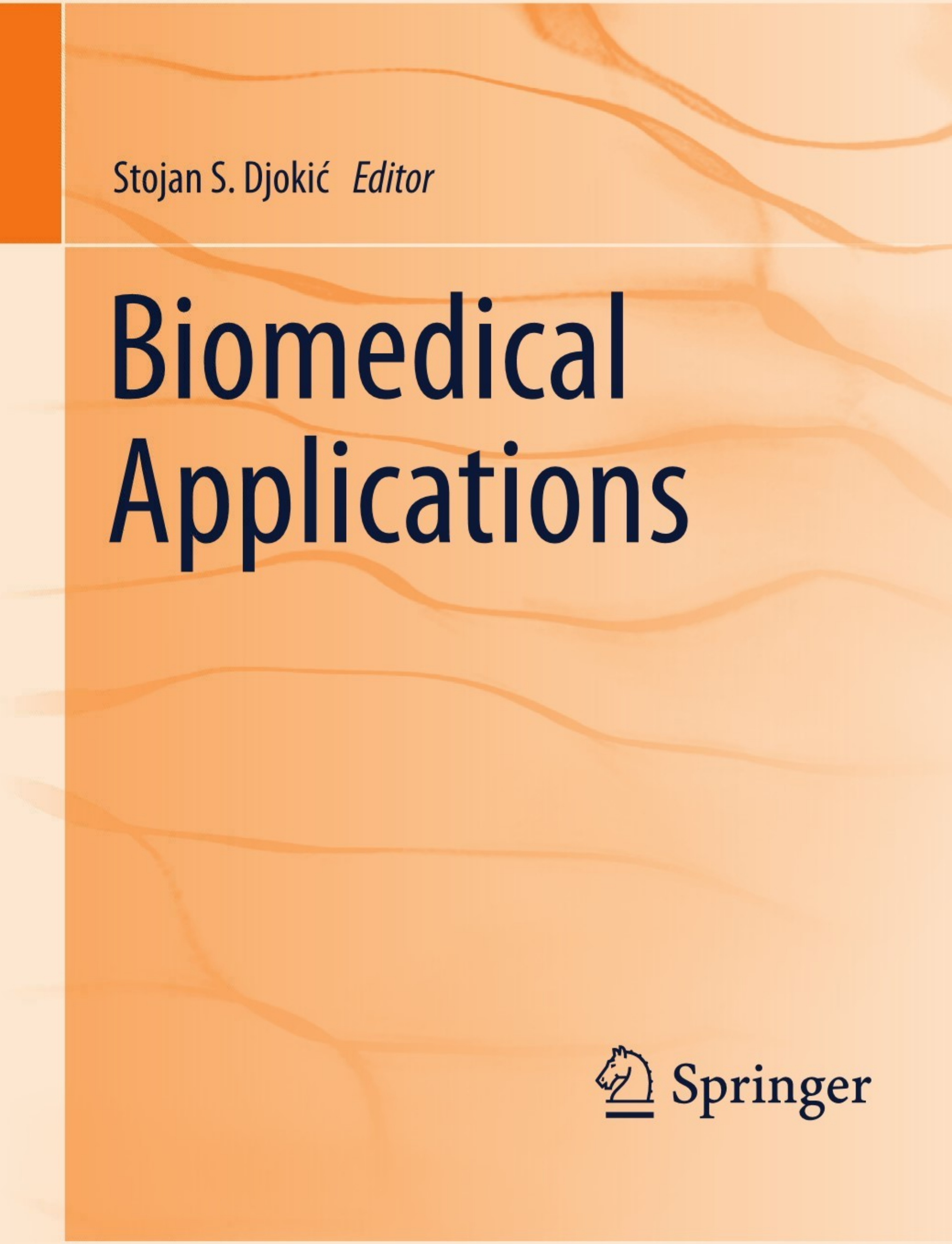
Modern Aspects of Electrochemistry 55



Stojan S. Djokić *Editor*

Biomedical Applications

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Preface

Research in electrochemical science and technology has brought about tremendous achievements. Beyond the traditional applications in electronics, energy devices, aerospace, and automotive areas, developments in electrochemistry are very important for many practical biomedical applications. In particular, developments related to medical devices, implants, sensors, antimicrobially active materials, drug delivery systems, etc. have significantly advanced in the past few decades.

The aim of this volume of Modern Aspects of Electrochemistry is to review the electrochemical aspects of the latest developments of various materials used in biomedical applications.

Competent scientists/researchers in their respective fields from all around the world were invited to write this volume.

In Chapter 1, by Ingrid Milošev, properties of CoCrMo alloy for biomedical applications are thoroughly analyzed. This alloy is one of the most important alloys used in orthopedic and dental implantology, due to its hardness, high wear resistance, and superior corrosion resistance under physiological conditions. The chapter discusses the electrochemical characterization of CoCrMo alloy under various conditions simulating physiological circumstances, and results in vitro and in vivo obtained thus far are critically evaluated. In addition, Milošev discusses in detail the tribocorrosion behavior of CoCrMo alloys, which is of tremendous significance for orthopedic implants. It is believed that this chapter will bring to the readers basic concepts and open a new window for future directions related to the biomedical applications of CoCrMo alloys.

Chapter 2 by Magagnin, Cojocaru, and Secondo is devoted to the exploitation of electroless methods for generating metallic nanostructures for biomedical technologies. Electroless deposition is a very viable route for the synthesis of metallic nanostructures. This chapter discusses electroless deposition of Au, Ag, Cu, Ni, Co, etc. for a number of biomedical applications. Applications to sensors and microdevices, preparation and use of nanostructured metals for supporting and wiring biomolecules for DNA analysis, and disease screening are discussed. The use of nanostructures, such as nanorods and nanoparticles, is analyzed in view of their potential applications to nano-biotechnology. Metallic nanostructures, developed via electroless deposition, may in the future play a fundamental role in the understanding of different interactions of biological systems at the nanolevel.

Sannakaisa Virtanen discusses corrosion behavior, surface modification, and biocompatibility of biodegradable Mg alloys in Chapter 3. Magnesium and its alloys are very attractive for applications as biodegradable implants, since they readily corrode in body fluids. On the other hand, the corrosion products, namely Mg(II) ions, are considered to be nontoxic. This chapter analyzes basic concepts of Mg corrosion vis a vis possible biomedical applications as implants. Hydrogen evolution, an increase in pH in the vicinity of the corroding surface, and nonuniform propagation of dissolution of Mg are analyzed. Importantly for the present volume of Modern Aspects of Electrochemistry, Virtanen discusses surface modifications in order to tailor the degradation and biological performance of Mg alloys. Conversion coatings, e.g., MgF_2, Ca-phosphate coatings, protein coatings, or self-assembled monolayers as possibilities for the surface modification of Mg alloys are analyzed.

Chapter 4 by Norman, Thakur, and Thundat provides an overview of the current literature on combined electrochemical–microcantilever measurements, which may have significant applications in the biomedical field. These devices have the potential to exhibit fast and reliable detection of small concentrations of molecules in biofluids. Nanoscale actuators are needed for a wide range of applications such as robotics, artificial muscles, prosthetic, micromechanical, and microfluidic devices. They can be operated under physiological conditions, making them particularly well suited for biomedical applications. As this chapter clearly states, in order to achieve improved performance for biomedical applications, development of microcantilever sensors that allow for measurements in complex real-life samples must be continued in the future.

In Chapter 5 by Djokić, treatments of various surfaces with silver and its compounds for biomedical applications are described. The antimicrobial properties of silver are well known. Silver or its compounds have been applied as coatings for devices used as topical wound dressings, urinary catheters, endotracheal tubes, cardiac valves, etc. In this chapter, electrochemical, chemical, and physical treatments of various surfaces with silver and their antimicrobial properties for biomedical applications are discussed.

This new volume of Modern Aspects of Electrochemistry brings to scientists, engineers, and students new concepts and summarized results related to surface treatments for biomedical applications, which may have significant influence for future practical applications.

Edmonton, AB, Canada Stojan S. Djokić

Contents

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Chapter 1
CoCrMo Alloy for Biomedical Applications

Ingrid Milošev

1.1 Introduction

Metallic materials used in biomedical applications have become increasingly important as the number of various implanted devices, e.g., orthopedic, cardiovascular, dental, and ophthalmological implants, constantly increases. In addition to titanium-based alloys and stainless steel, cobalt–chromium–molybdenum alloy (CoCrMo) is one of the most important materials used in orthopedic applications, i.e., total hip replacements. The increasing number of implanted hip replacements is the result of the prolongation of the average life expectancy and an active lifestyle in older age. Among the diseases of the joint that in most cases require surgical treatment, osteoarthritis is the most important. After implantation of a hip prosthesis, pain is reduced and the functionality of the joint is recovered. The average lifetime of the implanted prosthesis is about 15 years. Compared to implants used in the 1970s, the lifetime of contemporary hip prostheses progressively increases because of progress in surgical techniques, treatment, material manufacturing, and quality control. The ultimate goal is to produce hip prostheses

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that would endure the average postsurgical lifetime of more than 20 years and enable the patient to live an active lifestyle without pain. To achieve this goal, understanding alloy behavior in vitro and in vivo is crucial.

As metallic materials were introduced into biomedical applications in the 1940s–1950s, it was recognized that corrosion resistance is of special importance. Early in vitro studies were performed in saline and simulated physiological solutions, first mainly as static experiments. Retrieval studies soon showed that some corrosion or corrosion-initiated localized damage occurred at the metal components, and in vitro studies were then conducted in a way to study possible localized phenomena. In this chapter, the progress of early electrochemical studies is summarized. It was also recognized early that the passivity of an alloy to be used in the human body is based on the formation of a thin passive film, but its characteristics were not known in detail. As the applications of CoCr-based alloys in orthopedics intensified, the interest in these materials increased as well. More sophisticated electrochemical and surface analytical techniques were introduced in the late 1990s and 2000s. In this chapter, these studies are reviewed, including the most important results concerning the composition, structure, and thickness of the passive oxide layer formed at the CoCrMo alloy surface in simulated physiological solutions. The majority of results are related to simple saline simulated physiological solutions. The effect of phosphate ions is described in detail. It was recognized, however, that a simple saline solution does not entirely mimic in vivo conditions and that the effect of biomolecules should be taken into account. As a model for biomolecules, the effect of a complexing agent is discussed, followed by the effect of proteins, mainly albumin. The formation and distribution of organometallic compounds, as the most important compounds formed between metal ions and proteins in vivo, is presented. It becomes clear that to approach closely an in vivo situation, in vitro experiments should be conducted in media containing biomolecules and living cells.

Tribocorrosion experiments can be regarded as a bridge between the in vitro and in vivo situation. These experiments, conducted in various media with special emphasis on the change in wear mechanism caused by the presence of proteins, are presented. Finally, studies performed on retrieved metal components are described to identify the types of corrosion processes in vivo.

1.2 CoCrMo Alloys and Their Properties

1.2.1 Development and Chemical and Physical Properties of Cobalt-Based Alloys

Alloying of cobalt was developed most notably by E. Haynes at the beginning of the twentieth century. Haynes developed a series of cobalt–chromium alloys named Stellites [1]. In 1913, cobalt–chromium–tungsten alloys (CoCrW) were patented. In the 1930s the cobalt-based alloy Vitallium was patented and used for the manufacture of parts for aircraft engines. In the original specification, it contained 30% Cr, 7% W, and 0.5% C; later the tungsten was replaced by 5% Mo. A similar alloy was developed also by Krupp in Germany. The composition of these older alloys—Stellites, Vitallium, and HS—is given in Table 1.1. Molybdenum is added to refine grain size, enhance solid solution strengthening, and increase corrosion resistance. The composition of CoCrMo alloys has not changed significantly since that time. The largest change is related to the stricter control of the content of carbon and, consequently, the more homogeneous distribution of hard carbide grains and increased abrasion resistance of the alloy. There are six ISO 5832 (International Organization for Standardization) standards for Co-based alloys, which correspond to various compositions and manufacturing processes. Four of these are mainly used in orthopedics [2–5]. Today, the cast and wrought alloys ISO 5832-4 and 5832-12 are primarily used in orthopedics. According to the American Standards for Testing and Materials (ASTM) classifications, these alloys are denoted as F-75 and F-1537,

Table 1.1 Composition of original Co-based alloys [1]

	Composition/wt (%)								
Alloy	Co	Cr	Mo	Ni	Fe	Mn	W	C	Si
Stellite 1 CoCrW	50	33					13	2.5	
Stellite 8 CoCrMo	63	30	6					0.2	
Vitallium CoCrMo	62.5	30	5			0.5		0.5	0.2
HS-21 CoCrMoNi	Bal.	27–30	5–7	2–5	0.75	1		0.2–0.35	
HS-25 CoCrNi	Bal.	19–21		9–11	3	2		0.05–0.15	

respectively. These two alloys have almost identical composition but differ in microstructure. There are two types of wrought alloys, low- and high-carbon, which differ in carbon content. Other Co-based alloys include CoCrWNi and CoNiCrMo wrought alloys, but these alloys are less appropriate for use in orthopedics because of their poor wear properties [6, 7]. Moreover, these two alloys contain nickel, which raises concerns about biological reactivity.

Cast alloys have a chromium-rich matrix and larger grains. With hot isostatic pressing, the grain size can be reduced to 8 μm. Cast alloys exhibit an inhomogeneous, large-grained, cored microstructure. The dendritic regions are Co rich, whereas the interdendritic regions can be a quaternary mixture consisting of various Co-rich, Cr-rich, and Cr- and Mo-rich phases [1]. Wrought alloys have a face-centered cubic structure that exhibits an austenitic microstructure with finely distributed small block carbides.

Cobalt-based alloys are very tough materials. They can be described as wear- and corrosion resistant and are stable at elevated temperatures. Many properties stem from the crystallographic nature of cobalt, the formation of a solid solution with chromium and molybdenum, and consequent formation of extremely hard carbides [1, 7]. Co-based alloys exhibit relatively high density (8.9 $\mathrm{g\,cm^{-3}}$) and high elastic modulus (210–253 GPa). These properties are less attractive compared to Ti-based alloys, which exhibit lower density (4.5 $\mathrm{g\,cm^{-3}}$) and an elastic modulus (110 GPa) closer to that of bone. However, a combination of high corrosion resistance, wear resistance, high hardness (300–400 Vickers hardness), and ultimate strength (655–1,300 GPa) is the basis for the applications of Co-based alloys in joint replacements [7].

1.2.2 *Use of CoCrMo Alloys in Orthopedics*

In addition to its use in engineering, in the 1930s Vitallium was also used for the preparation of metallic dental casting as an alternative to gold alloys, which had already become very expensive [1]. Vitallium was introduced to orthopedics by Smith-Peterson in 1937 [1]. At about the same time, H. Bohlman, using the work of Venable and Stuck, designed a corrosion-resistant short stem made of Vitallium [7]. In 1938 Philip Wiles designed the first total hip arthroplasty made of stainless steel [2]. A steel ball was secured to the femur with a bolt and a stainless steel acetabular liner was secured with screws.

This design was rather disappointing because the stainless steel used at that time was insufficiently corrosion resistant. Long-stemmed prostheses appeared in the 1950s and provided less stress concentration. The design of the Wiles prosthesis was adopted in 1951 by G.K. McKee and J. Watson-Farrar, at first using stainless steel, and later a CoCrMo alloy. This design was a so-called metal-on-metal combination comprising a metal femoral head articulating within a metal acetabular inlay. The cast CoCrMo alloy was considered satisfactory for total hip replacements [8]. In the mid-1960s, poly(methyl methacrylate) (PMMA) cement was used for fixation in hip arthroplasty for the first time. The relatively high torque and frictional forces resulted in the generation of metallic debris and early loosening. In 1960, John Charnley developed a "low friction" arthroplasty using an acetabular shell made of polytetrafluoroethylene (PTFE, Teflon). Unfortunately, this design resulted in early failures because of the poor wear resistance of PTFE. Charnley then replaced PTFE with high-density polyethylene, which was not as friction free as PTFE but much more wear resistant. The femoral component was made of stainless steel and had a 22-mm head [9]. The prototype of this prosthesis was developed in 1962 and still remains the gold standard of hip arthroplasty with metal-on-polyethylene articulation. The basic Charnley design was later modified by Muller (so-called Charnley–Muller prostheses) [10]. Stainless steel was replaced by CoCrMo alloy, and the prostheses had a variable neck size and larger head size. The Charnley prosthesis, which was the basic archetype, was followed by hundreds of different designs and modifications. In the past 15 years, CoCrMo alloy has been mainly used as a bearing surface, i.e., for the manufacture of the femoral head in metal-on-polyethylene bearings where it articulates against the interior of a polyethylene cup, and for the manufacture of femoral head and acetabular inlay in metal-on-metal bearings of total joint replacements and surface replacements.

1.3 Early In Vitro Investigations and Relationship to In Vivo Failures

The high corrosion resistance of a metal or alloy to be used in the human body as a dental or orthopedic implant was immediately recognized as one of the most important prerequisites. "High strength materials with extreme inertness are required," as was noted by Hoar and Mears [11]. None of the implant materials is perfect in the sense of fulfilling all mechanical, chemical, and safety requirements completely. Because body fluids, such as blood, plasma, and lymph, all contain a considerable concentration of chloride ions, it was important to recognize under which conditions the breakdown of passivity may occur in vivo [11]. The authors emphasized that "even if no visible breakdown occurs, i.e., the metal is in the passive state, perhaps in many years in vivo transfer of metal to surrounding tissue may be appreciable" [11].

Hoar and Mears investigated various stainless steel, CoCrMo, and Ti-based alloys in 0.17 M NaCl and Hanks' physiological balanced salt solution [11]. Hanks' "physiological" or balanced salt solution fairly closely imitates (from the chemical aspect) the fluid in muscle and bone [12]. Resting potentials (potential of an isolated specimen after 480 h in stagnant solution open to the air) and breakdown potentials (at which the anode showed a sharp increase of current when potential was gradually raised) were measured. Stainless steels exhibit breakdown potentials ~50–150 mV below the resting potential. Thus, film breakdown can always be expected where these alloys are used in aerated solutions of 0.17 M chloride content. The resting potential for Vitallium was 0.5 V, far less negative than the breakdown potential at 0.87 V. Thus, film breakdown is very unlikely. Titanium alloys exhibit breakdown potentials >6 V, which is far more positive than the resting potential in the range of 0.3–0.5 V. However, under abrasion, scratching, or crevice conditions, healing of the oxide layer by repassivation may take some time. In a crevice, the long and narrow electrolytic path between it and the surface cathode may lead to such a large ohmic drop through the solution that its repassivation is not possible. The authors concluded that stainless steels (even of the higher Cr–Ni quality) are "unlikely to resist all breakdown by pitting when exposed to the body fluids (or other media containing chloride) indefinitely; cobalt-based alloys may well withstand such exposure for long times; titanium and (especially) some of its alloys should withstand such exposure for an indefinite period" [11].

A.T. Kuhn reviewed corrosion of CoCr alloys in aqueous environments, among them also physiological media (0.9% NaCl and Ringer's solution) [13]. The literature data were divided into the following categories: simple corrosion, stress corrosion, crevice corrosion and pitting, fretting corrosion, couple corrosion, and corrosion in vivo. Various CoCr alloys (Wironit, Vitallium, and Wironium) that were immersed for 2 months in solution containing 9 g l^{-1} NaCl in an open beaker at 37°C showed only minimal corrosion (less than 0.2 ppm) [14]. Although the alloy was not susceptible to stress corrosion, crevice and pitting corrosion were observed. Co-based alloys become more susceptible to crevice corrosion as Ni content increases from 0% to 25%. Alloys with at least 20% Cr were more crevice attack resistant when Mo content was 5% or more. The resistance of Co-based alloy to pitting was high [15], but fretting corrosion may harm the passive oxide layer.

Corrosion rates of metals in vivo based on the concentration of metal ions in surrounding tissue after implantation in animals are much higher than in vitro [16, 17]. This conclusion was achieved by the authors presumably for two reasons. The first reason is chemical; i.e., the composition of the environment is more corrosive than that found in a simulated physiological solution. The second reason is that crevice conditions are somewhat established by the surrounding tissue. Therefore, in the following studies the occurrence of possible corrosion processes under specific circumstances, e.g., crevice and galvanic corrosion, was investigated in more detail. Alloys of cast CoCrMo, wrought CoCrMo, wrought CoNiCrMo, and Ti–6Al–4V alloys were incorporated in specimens simulating couple and crevice corrosion conditions [18]. The specimens were implanted in dogs for 30 months. No substantial evidence of corrosion activity on the surfaces of the metal was observed, except for a tarnish film on the titanium alloy when coupled to a cast CoCrMo alloy. Because the tarnish film was not observed in vitro, the authors concluded that in vitro studies alone are not completely definitive and that a prosthetic device which is a composite of the cast CoCrMo and Ti–6Al–4V alloys may be inappropriate [18].

The use of combinations of dissimilar metals in multi-alloy hip prostheses leads to conditions in which galvanic corrosion may appear. To check this possibility, cyclic polarization curves were measured for individual and coupled CoCrMo and Ti–6Al–4V alloys in 0.9% NaCl [19]. Galvanic coupling did not significantly enhance corrosion tests. The resistance of CoCrMo alloy to pitting and crevice corrosion was even improved by coupling to titanium alloy. No exaggerated corrosion caused by the coupling was noted on retrieved Sivash prostheses that incorporated both these alloys [19]. Based on potential versus time curves measured in isotonic saline solution of low pH (1.5) to accelerate corrosion, a conclusion was reached that CoCrMo alloys should not be used in combination with stainless steel but may be used in combination with titanium alloy [20]. The specimens were fabricated from a CoCrMo alloy (HS21) cylinder force fit in a large titanium alloy, or a stainless steel cylinder, to give a surface-to-area ratio of 1:4 and a crevice between metals. As similar results were obtained by other authors [21, 22], it was concluded that the corrosion rate in a stable passive region is not significantly increased by coupling; thus, what is of interest is how coupling affects the resistance of the alloys to pitting or accelerated general corrosion, i.e., to local or general passive film breakdown.

Potentiostatic polarization curves for individual specimens in 0.9% NaCl (pH 7) showed that stainless steel is very susceptible to pitting [21]. No pitting was observed for Co- and Ti-based alloys, although the Co-based alloy indicated possible susceptibility to pitting or crevice corrosion [21]. Lucas et al. investigated susceptibility of surgical CoCr alloy to pitting corrosion in vitro and in vivo [23]. The in vitro study comprised cyclic polarization curves in 0.9% NaCl at 37°C at pH 7.0 under both aerated and deaerated conditions. Current hysteresis, as a typical feature of pitting corrosion according to the protection potential theory, was observed only for alloy passivated in phosphoric acid, but not for a nonpassivated alloy. However, no evidence of pitting corrosion was revealed. Also, the examination of the nonbearing surface of hip prostheses made of cobalt alloy after in vivo implantation up to 6 years showed no features uniquely identified as the result of pitting corrosion. Casting microporosity was observed on retrieved femoral heads, which could mistakenly be identified as pitting corrosion. Because passivating treatment either changed the surface chemistry of the oxide layer or increased it, it was hypothesized that current hysteresis is related to the breakdown of this preestablished passive film followed by a repassivation. This behavior should not be associated with pitting corrosion as is normally taken to be the case by application of the protection potential theory. Based on these results, it was concluded that CoCrMo alloy will not undergo pitting under static conditions. However, when the alloy is either severely cold worked or subjected to fretting or a cyclic loading condition, pitting corrosion has been observed in vitro [24, 25].

Forged CoCrMo alloy exhibited higher resistance to pitting and crevice corrosion in media containing chlorides than cast alloy, which was ascribed to a more homogeneous and finer-grained structure [26]. This alloy also exhibits total resistance to stress corrosion cracking in the elastic and even plastic range. Under movements of parts made of forged and cast alloys, no galvanic corrosion was observed, as both the cast and forged alloys remained in the stable passive state.

1.4 Electrochemical Studies on Individual Metals in Simulated Inorganic Physiological Solution

In their early study, Hoar and Mears emphasized that the extremely slow release of cobalt and titanium into the surrounding environment is caused by the passage of cations through their passivating oxide film, without breakdown [11]. It was also noted that all the alloys protect themselves by formulation of a passive film [27]. In this chapter the properties of the passivating oxide layer formed on CoCrMo alloy under simulated physiological solution in the light of more recent studies and sophisticated electrochemical and surface analytical techniques are discussed. First, electrochemical behavior of the individual metal components—Co, Cr, and Mo—of the CoCrMo alloy is presented. The effect of the presence of chloride ions, which are abundantly present in simulated physiological solutions, is also discussed. Then, the results for the CoCrMo alloy are presented, accompanied by discussion of the effect of particular metal components.

1.4.1 Electrochemical Studies on Cobalt

Cyclic voltammograms (CVs) for Co metal recorded in 0.9% NaCl (NaCl), simulated Hanks' physiological solution (SPS), and phosphate buffer solution (PBS) are depicted in Fig. 1.1. The composition of the solutions used is given in Table 1.2. CVs recorded in chloride-based solutions—NaCl and SPS—are very similar, with much shorter passive range compared to nonchloride-containing phosphate buffer. Let us first discuss the behavior in the latter solution. The CV shows typical features of anodic behavior of cobalt in alkaline solutions, which is relatively complex and depends on the potential range. It can be divided into active dissolution, passivity, transpassivity, and oxygen evolution [30, 31, 43–47]. At pH 7–10, the primary passivity is caused by the formation of CoO or, more likely, the hydrated oxide, $Co(OH)_2$:

$$\begin{aligned} &\mathrm{Co} + 2\mathrm{H_2O} \rightarrow \mathrm{Co(OH)_2} + 2\mathrm{H^+} + 2\mathrm{e^-}, \\ &E_0 = 0.166 - 0.0591\ \mathrm{pH}\ (\mathrm{SHE}) \end{aligned} \tag{1.1}$$

The shape of active/passive transition (the height of the anodic peak) and the extent of the passive region are dependent on the