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The use of electrochemical techniques to evaluate the corrosion performance of metallic biomedical materials and devices

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Abstract: The corrosion performance of metallic biomedical materials and devices is commonly evaluated using electrochemical techniques. Although test standards involving such techniques have been released to address some forms of corrosion, a key issue is application of the results with regard to use of an implantable device in vivo. This review focuses on nitinol, 316L/LVM stainless steel, and Co–Cr alloys and is intended to provide some perspective on the significance of results from tests concerning general corrosion, localized corrosion, galvanic corrosion, and fretting corrosion of these alloys in simulated physiological solutions. It also examines the factors that could cause differences in the corrosion performance between in vitro and in vivo exposure, with the goal of providing some rationale for applying electrochemical characteristics obtained from the tests to predict the corrosion performance in vivo. © 2018 Wiley Periodicals, Inc. J Biomed Mater Res B Part B: 00B: 000–000, 2018.

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INTRODUCTION

Electrochemical techniques are widely used to study the corrosion performance of metallic biomedical materials and devices. In many cases, the techniques are directed toward determining whether an implantable device has adequate corrosion resistance for use in vivo. In other cases, they have been used to examine the electrochemical behavior of a metallic biomaterial, particularly with regard to interactions between the material and chemical components in the physiological fluid of interest.

Although test standards have been issued for a few forms of corrosion, application of the results remains open to some question in terms of how to view them and what values represent suitable limits for use of an implantable device in vivo. In addition, the tests are generally performed in simulated physiological solutions rather than actual physiological liquids. The simulated solutions are based primarily on the salt content of the actual physiological solution, so they may lack proteins or other organic components that can influence corrosion through processes such as adsorption and complex formation.

This review examines the use of electrochemical techniques for evaluating the corrosion performance of metallic biomedical materials and devices in simulated physiological solutions. It is intended to provide some perspective on the significance of results from tests concerning general corrosion, localized corrosion, galvanic corrosion, and fretting corrosion in simulated physiological solutions. The focus is on the electrochemical characteristics obtained from these tests and the factors that could cause differences in these characteristics between in vitro and in vivo exposure, with the goal of providing some rationale for applying the characteristics to predict the corrosion performance in vivo.

Potentials in corrosion studies of metallic biomedical materials and devices are typically reported with respect to a saturated calomel electrode (SCE) or silver/silver chloride electrode. Unless otherwise stated, the potentials cited in this review are referenced to an SCE.

PHYSIOLOGICAL FLUIDS

Corrosion tests involving metallic biomedical materials and devices, as noted above, are usually performed in simulated physiological solutions rather than actual physiological fluids. The choice of test solution in the case of a device is determined to a large extent by where the device will be implanted.

Blood

Several solutions are commonly used to simulate blood in corrosion tests: saline (0.9 wt % NaCl), Ringer's solution, Hanks solution, and phosphate-buffered saline (PBS). The simplest one is saline. The other three solutions all contain additional chlorides but differ with regard to other salts.[1] The standard Ringer's solution contains only chlorides, but

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phosphate and bicarbonate are often added for pH control. Unbuffered saline tends to be more aggressive than PBS[2], Ringer's solution (with phosphate),[3] and buffered saline (pH 7).[4] The difference would appear to be associated with the buffering capability. However, the buffering agents in the saline (pH 7) were not given, so the difference could also be related to the presence of phosphate which is known to adsorb on the surface of Ti,[5–7] nitinol,[8,9] and Co–Cr alloys.[10,11]

Both Hanks and Ringer's solutions can undergo considerable changes in pH when they are deaerated with nitrogen.[12,13] For instance, deaeration of Hanks solution was found to change the pH from 7.4 to about 8.5 and cause precipitation of calcium and magnesium carbonates. The pH of Ringer's solution can increase even more, reaching 9.0. In contrast, deaeration of PBS causes little change in the pH. Deaeration is intended to remove oxygen, so a CO_2/N_2 gas mixture can be used to deoxygenate Hanks and Ringer's solutions. The presence of $NaHCO_3$ at a concentration of 1.35 g/L in Ringer's solution or 1.45 g/L in Hanks solution, together with a 5% CO_2/N_2 mixture can provide both buffering at pH 7.4 and concentrations of bicarbonate and CO_2 similar to physiological values.[1,13]

For some tests, it is desirable to maintain oxygen at a physiological concentration in the test solution. Aeration of the solution, either by static exposure to air or by sparging with air, can be used as a reasonable approximation in such tests. The equilibrium potential (E_e) for oxygen reduction at 37°C is given by

$$E_e = E^o - 0.062pH + 0.015\log P_{O_2} \quad (1)$$

where, E^o is the standard electrode potential (1.217 V at 40°C)[14] and P_{O_2} is the partial pressure of oxygen. The value of P_{O_2} can range from 0.05 to 0.13 atm in blood,[13,15] which compares with 0.2 atm in air. These values correspond to differences in E_e between air and blood of only 3–10 mV. If the principal cathodic reaction of the corrosion process is assumed to be oxygen reduction, any difference in E_{corr} will therefore be small. Bubbling an oxygen-containing gas (air or some other mixture) through the solution during the test not only allows the dissolved oxygen to be maintained at a constant level in the bulk solution but also assists the diffusion of oxygen to the metal surface.

Bile

Two bile solutions—ox bile and human simulated bile—are given in ASTM Standard F2129.[1] The ox bile solution involves unfractionated dried bovine bile and is intended to have a pH of 6.5. The human simulated bile involves lactated Ringer's irrigation with the addition of cholic acid and several of its derivatives, as well as glycine and sodium hydroxide. The desired pH of this bile solution is 8.5 ± 0.2.

Urine

The compositions of two artificial urine solutions are listed in ASTM Standard F2129.[1] Both solutions contain chlorides and other inorganic salts. However, one solution contains citrate and oxalate, whereas the other solution contains urea and creatinine.

Saliva

Several studies have used a similar composition of artificial saliva.[16–18] In all these studies, the solution contains chlorides, diphosphate, sodium sulfide, and urea, with only slight differences in two components ($CaCl_2 \cdot 2H_2O$ and $NaH_2PO_4 \cdot 2H_2O$).

GENERAL CORROSION

General corrosion of metallic biomedical materials and devices is generally evaluated in terms of corrosion potential (E_{corr}) or corrosion current (I_{corr}), which can be expressed as a corrosion rate. Immersion tests to measure E_{corr} of implantable devices are usually performed in accordance with ISO Standard 16429.[19] In these tests, E_{corr} and often the concentration of dissolved metal ions are monitored as a function of time.

A number of electrochemical studies have been directed toward obtaining I_{corr} for metallic biomaterials,[20,21] but a standard test method specific to implantable devices has yet to be developed. I_{corr} can be determined for not only biomaterials but also implantable devices using the Tafel extrapolation method. If evaluation of I_{corr} is based on the anodic Tafel region, the test method in ASTM F2129 can be adopted as described except that a lower potential limit can be used for the potentiodynamic scan. I_{corr} can also be obtained indirectly by using the linear polarization method to determine the polarization resistance (R_p), but the calculation of I_{corr} from R_p requires a knowledge of the Tafel slopes. This method has the advantage that it allows I_{corr} to be monitored as a function of exposure time for each sample.

Another technique, electrochemical impedance spectroscopy (EIS), has been used in a number of studies to examine the electrochemical behavior of biomedical materials in simulated physiological solutions.[22] Data for these materials are typically analyzed in terms of equivalent circuits containing one or two parallel combinations of a resistance and a constant phase element (CPE), which is commonly used in place of a capacitance to account for nonideal capacitive behavior. Values of R_p have been determined for biomaterials also by using EIS.[23–25]

Many of the tests conducted to obtain corrosion rates have involved simulated physiological fluids without organic components, such as proteins found in blood. However, phosphate and one such protein—albumin—have been shown to undergo competitive adsorption on Ti in Hanks solution[26] and Co–Cr–Mo in PBS.[10] Phosphate acts as an anodic inhibitor, whereas albumin limits adsorption of phosphate but can act as a cathodic inhibitor.[10] In the case of Co–Cr–Mo at E_{corr}, albumin completely suppresses the effect of phosphate. Notwithstanding such findings, the proteins in blood may actually have little overall effect on the corrosion rate of metallic implant materials in blood. Hoar and Mears reported that the passive current densities of Ti, 316 stainless steel, and Co–30Cr–6Mo in human blood were very similar to those in a 0.17 *M* NaCl solution and Hanks solution.[27]

A point to note, however, is that sodium citrate was used as an anticoagulant, and it has been shown to affect the passivation behavior of Co–Cr–Mo alloys[28] and stainless steels[29] by acting as a complexing agent. Such an effect could occur also in the case of Ti and its alloys, so the sodium citrate could have possibly masked effects of the blood components.

Tests to determine I_{corr} are often performed under deaerated conditions. Although such a situation is not representative of in vivo conditions, biomedical alloys are passive, and the corrosion of passive alloys occurs under anodic control.[30] Tests on, for example, electropolished (EP) nitinol showed that I_{corr} was governed by the anodic reaction.[31] Hence, aeration should not increase I_{corr} above the passive current density in tests with nitinol or other biomedical alloys.

A key issue is how to assess the magnitude of I_{corr} in terms of metal ion release. For EP or passivated alloys, the passive film has been grown such that I_{corr} can be expected to largely represent the rate of metal ion release. In the case of EP nitinol, I_{corr} was shown to be associated entirely with Ni^{2+} dissolution, which appears to be controlled primarily by solid-state mass transport of Ni^{2+} through the oxide film.[31]

To provide some perspective on the magnitude of Ni^{2+} release, the release rates are often compared with dietary intake levels. Thierry et al., for example, reported that Ni dissolution rates for nitinol were almost 1000 times smaller than the average Ni dietary intake,[8] which has been variously estimated as 160–900 μg/day[32] and 200–300 μg/day.[33] However, only about 1% of the Ni from food is absorbed in the body.[34] Moreover, as noted by Thierry et al.,[8] Ni^{2+} released in soft tissue may bind to blood plasma protein and only gradually be processed metabolically or eliminated from the body.[35] Also, local increases in the Ni^{2+} concentration may occur in the tissue surrounding the implant, especially if more severe forms of corrosion (e.g., pitting) are involved.

A similar comparison with dietary intake levels can be made in the case of Cr^{3+} release. Thierry et al. found that Cr dissolution from 316L stainless steel decreased to a nondetectable level over 3 days, but even the initial rate was almost four times lower than that of Ni.[8] Their study indicates that Cr dissolution rates are far lower than the adequate dietary intake for Cr, which has been set as 25–35 μg/day based on estimated mean intakes.[36] However, only a small percentage (0.4%–2.5%) of Cr, like Ni, is actually absorbed in the body,[36] and Cr can also bind to blood proteins.[37]

LOCALIZED CORROSION

Methods

The susceptibility of metallic biomedical materials and devices to localized corrosion is generally evaluated using cyclic potentiodynamic polarization, as described in ASTM Standard F2129, Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements to Determine the Corrosion Susceptibility of Small Implant Devices.[1] The tests are typically performed in a simulated physiological solution, and the resulting polarization curves allow values of the breakdown potential (E_b) and repassivation, or protection, potential (E_R) to be determined for the material or device in that solution. In many cases, E_R cannot be determined because pits that would be available for repassivation were not formed during the forward scan or because pit (or crevice) repassivation did not occur during the reverse scan.

Another method for evaluating localized corrosion involves the use of a sequence of potential steps to determine E_b. The test method is described in ASTM Standard F746, Standard Test Method for Pitting and Crevice Corrosion of Metallic Surgical Implant Materials, which focuses on metallic materials used for surgical implants rather than on the implants themselves.[38] Difficulties can occur with application of this method, because stepping to a given potential may initially cause localized corrosion but then fail to do so after several steps to that same potential.[39]

The potentiostatic scratch method has also been used to determine E_b for metallic biomaterials.[40,41] This method gives a value of E_b that is independent of surface finish but may therefore not be representative of the undamaged surface. The surface in the scratched area could in fact be quite different from that produced by a treatment such as electropolishing or passivation, particularly with regard to inclusions. Pitting appears to initiate at inclusions in EP nitinol[42–44] and 316 stainless steel.[45,46] Exposure to a higher concentration of possibly larger inclusions in the scratched area means that the value of E_b obtained by the scratch method may not accurately reflect the pitting resistance of an alloy with a treated surface.

The susceptibility of a metallic material to pitting corrosion in a particular environment can be characterized in terms of E_b relative to E_{corr} (or E_r in ASTM F2129 terminology).[47–52] The difference between E_b and E_{corr}, rather than E_b itself, reflects the likelihood of pitting and so is commonly used as a measure of the alloy's susceptibility to pitting corrosion. In effect, E_b–E_{corr} represents the margin of safety for pitting.[50,51] Stainless steels in aerated chloride solutions often exhibit similar values of E_{corr}, and as noted by Sedriks, it has become common to equate pitting resistance to E_b alone, rather than to E_b–E_{corr}.[52] However, evaluation of pitting resistance based solely on E_b can be misleading in cases where the alloys differ in their values of E_{corr} or, if they have similar values initially, in their variation of E_{corr} with time.

No consensus has been reached on what value of E_b–E_{corr} constitutes a suitable threshold for use of an implantable device in vivo. ASTM Standard F2129 recommends comparing the test device with a reference device that has a history of good corrosion resistance in vivo. This type of comparison has been made for nitinol devices, although it is based solely on values of E_b.[53] Devices with an E_b of 0.5 V or higher were considered to have a sufficiently high corrosion resistance when compared with the stainless steel Palmaz–Schatz stent, which has the longest implant history. However, comparison of E_b–E_{corr} values would be more appropriate, particularly since it would allow for differences in E_{corr} between stainless steel and nitinol.

Criteria were proposed by Corbett to define boundaries for acceptable E_b values (>0.6 V) and unacceptable E_b values (<0.3 V) in PBS at 37°C.[12] A device was considered to be in its optimal corrosion-resistant condition if E_b exceeded 0.6 V, but not if E_b was less than 0.3 V. These criteria can be useful, since they reflect the degree to which the design, manufacturing, and surface finish are optimized. However, Rosenbloom and Corbett later tied these values more directly to corrosion performance, whereby a material was considered to have acceptable corrosion resistance if the material consistently exhibits resistance to breakdown at or above 0.6 V.[54] Material that exhibits breakdown potentials below 0.3 V was considered unacceptable. These values, however, are not specific to a particular material or device and hence do not allow for differences in E_{corr} between materials or surface treatments; E_b–E_{corr} is recognized in the corrosion field as providing a more valid measure of pitting corrosion resistance.[48–52]

The criteria proposed by Rosenbloom and Corbett also appear to be unnecessarily conservative. They were based in part on E_{corr} values reported by Hoar and Mears,[27] but Rosenbloom and Corbett apparently overlooked the fact that these values were relative to the normal hydrogen scale. Adjustment of the E_{corr} values to the SCE scale might have led to lower values of E_b for the acceptance criteria. The conservative nature of the criteria was borne out in cyclic polarization tests performed on marketed vascular devices with no reported history of corrosion issues.[55] There appeared to be no correlation between clinical performance and in vitro test results, based on the E_b values proposed by Corbett and Rosenbloom. Breakdown was found to occur below 0.3 V for some devices, even though these devices reportedly were clinically proven to have adequate corrosion resistance. Moreover, almost none of the nitinol devices would be predicted to survive to 0.6 V, suggesting that this threshold was unreasonably high. Pértile et al. in fact suggested, on the basis of in vivo E_{corr} values, that nitinol should not be susceptible to breakdown as long as E_b remains above 0 V.[56] This threshold, however, depends on E_{corr} and may not be high enough in some cases, because stents that had E_b values of up to about 0.1 V have been found to exhibit pitting on explants.[57]

The use of E_R for evaluating the corrosion performance of implantable devices has been limited, although it has been cited as a measure of their susceptibility to crevice corrosion.[1,58] This concept was developed by Wilde and Williams on the basis of potentiostatic tests involving 430 stainless steel with an artificial crevice in aerated 3.5 wt % NaCl.[59] Samples polarized above E_R exhibited crevice corrosion with no evidence of pitting, whereas samples polarized below E_R showed no corrosion. In subsequent work, Cahoon et al. suggested that the difference in crevice corrosion resistance of two implant alloys (Co–28Cr–6Mo and 316L stainless steel) was related to their values of E_R determined from cyclic polarization tests.[58] However, E_R is usually associated with repassivation of pits in such tests, and its value has been shown to vary with the extent of pit propagation, so the use of E_R should be treated circumspectly.[47]

Alloys

Nitinol. Values of E_b and E_b–E_{corr} for nitinol in simulated physiological solutions are given in Table I. A more comprehensive list of values is presented elsewhere.[20] The values in Table I are representative of different surface finishes with a focus on stents, although a few wire and disk samples are included for comparison. In most cases, the pre-scan immersion time was 1 h, but where a shorter time (≥0.5 h) was used, E_{corr} was generally reported to have reached a stable value. Figure 1 groups the E_b–E_{corr} values according to surface finish. It is notable that, even for heat-treated nitinol, E_b–E_{corr} can be relatively high, with values approaching 0.6 V in some cases. Trépanier et al., for example, obtained an average E_b value of 0.1 V for untreated (heavily oxidized) stents in Hanks solution, but E_{corr} was typically about −0.5 V and so the average E_b–E_{corr} value was approximately 0.6 V.[60] Values of E_b–E_{corr} in the region of 0.6 V were likewise obtained by Warner for stents made from EP nitinol wire that was heat-treated in air to form a thermally grown oxide.[61]

Mechanical polishing generally results in values of E_b–E_{corr} that are considerably higher than those obtained for heat-treated samples. In one study, MP stents were reported to have an average value of over 0.8 V in PBS, whereas heat-treated stents had average values of 0.2–0.3 V.[57] The majority of studies involving MP nitinol in PBS and Hanks solution have in fact found that E_b–E_{corr} exceeds 0.8 V.[20] In many cases, breakdown did not even occur at potentials up to 0.8 V or higher.

Surface treatment in the form of electropolishing or passivation markedly improves the resistance of metallic biomedical materials and devices to localized corrosion.[2,8,60] Electropolishing, for example, has been shown to increase the resistance relative to that obtained with mechanical polishing.[2,8] Numerous studies have found that EP nitinol in wire and disk form was resistant to breakdown in PBS and Hanks solution at potentials up to over 0.8 V, resulting in E_b–E_r values above 1 V.[2,8,67–69] Implantable devices made of EP nitinol also typically show a high resistance to breakdown. Wohschlögel et al. performed potentiodynamic polarization tests on devices ranging from small neurovascular stents to large heart valve frames in deaerated PBS.[70] Breakdown was found to occur below 0.8 V on only about 3% of 975 small devices. Larger devices showed a greater propensity to breakdown, with about 6% of 280 samples breaking down below 0.5 V and 16% below 0.8 V. However, E_{corr} was typically −0.35 to −0.15 V for the devices (large and small), so 94% of large devices had E_b–E_{corr} values of at least 0.65 V. A device with such a value would be unlikely to undergo pitting corrosion at open-circuit in a deaerated simulated physiological solution or, as discussed later, an actual physiological fluid, even allowing for the presence of oxygen in vivo.

Stainless steel. 316L/LVM stainless steel, like nitinol, exhibits a range of values for E_b–E_{corr}, as shown in Table I. A more comprehensive list of values is given elsewhere also for 316L/LVM stainless steel.[21] The values in Table I are representative of different surface finishes for various types of samples. Figure 2 compares the E_b–E_{corr} values for

TABLE I. Potentials From Potentiodynamic Tests on Nitinol and 316L/LVM Stainless Steel in Simulated Physiological Solutions[a]

Samples	Finish	Solution	E_{corr} (V)[b]	E_b (V)	E_b–E_{corr} (V)	References
Nitinol						
Stent	Untreated (oxidized)	Hanks	~–0.5[c] at 0.5 h	0.1	~0.6	60
Stent	Heat-treated	PBS	–0.141 (0.044)	0.111 (0.063)	0.252 (0.090)	57
	Air-furnace Oxidized tube		–0.230 (0.178)	0.068 (0.029)	0.297 (0.165)	
Stent	Heat-treated after EP	PBS	–0.106 (0.023) at 1 h	0.446 (0.148)	0.553 (0.150)	61
			0.036 (0.021) at 672 h[d]	0.680 (0.149)	0.644 (0.152)	
Stent	MP	PBS	–0.103 (0.065)	0.767 (0.225)	0.870 (0.240)	57
Stent	Non-EP	PBS	–0.180 at ≥0.5 h	0.4	0.58	62
	EP		–0.330 at ≥0.5 h	>1.0	>1.3	
Wire	MP	PBS	–0.294 (0.042)	0.381 (0.076)	0.675 (0.082)	2
	EP		–0.354 (0.022)	>1.1	>1.45	
Disk	MP	Hanks	–0.29[c]	0.53 (0.42)	0.82	8
	EP		–0.36[c]	>0.99 (0.05)	>1.35	
Stainless Steel						
316L plate	Untreated	PBS	–0.25[c] at ≥0.5 h	0.50[b]	0.75	62
316L flat	MP	Hanks	–0.21[c] at 24 h	0.28[b]	0.49	63
		MEM[e]	–0.21[c] at 24 h	0.40[b]	0.61	
316L disk	MP	Hanks	–0.43[c]	0.41 (0.05)	0.84	8
316L flat	MP	Hanks-type	~–0.55 [n]	0.428–0.448	~0.98–1.00	40
316L stent	EP	PBS	–0.338 at ≥0.5 h	>1.0	>1.3	62
316[f] stent	EP	Hanks	–0.040 (0.008)	>0.9	>0.94	64
316LVM wire	As-drawn	PBS	–0.081 (0.066) at 1 h	0.613 (0.099)	0.694 (0.127)	61
			0.033 (0.038) at 66 h[d]	0.961 (0.038)	0.928 (0.089)	
316LVM wire	As-drawn	PBS	–at ≥1 h	0.675 (0.185)	–	55
				0.518 (0.175)[g]		
316LVM flat	MP	Hanks	–0.39[c]	0.16	0.55	65
316LVM disk	MP	PBS	–0.45[c] [n]	0.36	0.81	66

[a]Where available, values shown are arithmetic mean (standard deviation).
[b]Measured after immersion for 1 h or when a stable value was obtained. The immersion time is shown, if different from 1 h, or marked as "[n]," if not reported.
[c]Estimated from potentiodynamic polarization curve.
[d]Results were obtained for two pre-scan immersion times.
[e]Eagle's minimum essential medium.
[f]The specific grade of 316 stainless steel was not reported.
[g]Two formulations of PBS were used: ASTM and Dulbecco's, respectively.

stainless steel in PBS and Hanks solution. As with nitinol, E_b–E_{corr} for an untreated surface can be relatively high. In the case of 316L plates (apparently untreated) in PBS, E_b–E_{corr} was shown to be roughly 0.75 V.[62] Other work similarly found that E_b–E_{corr} for as-drawn 316LVM wire in PBS was about 0.7 V, which increased to over 0.9 V with an increase in immersion time from the standard 1h to 66 h.[61] The E_b value for the 1-h immersion was 0.613 V, which compares reasonably well with the values (0.518 and 0.675 V, depending on the exact PBS formulation) obtained for as-received 316LVM wire in another study.[55] The corresponding values of E_{corr} were not reported in this other study, but the E_b values suggest that E_b–E_{corr} again would have approached or exceeded 0.7 V.

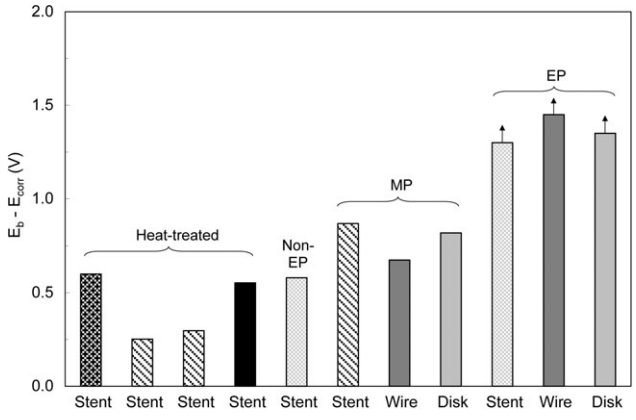

FIGURE 1. Typical values of E_b–E_{corr} for nitinol in simulated physiological solutions (PBS and Hanks). Samples are grouped by surface finish. Corresponding samples with different finishes in a particular study are indicated by bars with the same shade or pattern. Arrows indicate that the actual values are higher than shown by the bars.

Most studies have shown that E_b–E_{corr} for MP 316L/LVM stainless steel in PBS, Hanks and Ringer's solutions is typically at least approximately 0.5–0.6 V.[21] As in the case of nitinol, surface treatment is expected to result in higher values of E_b–E_{corr}. Passivation using HNO_3 has in fact been found to increase E_b for MP 316LVM plates by about 100–200 mV, depending on the acid concentration.[71] In addition, studies have shown that EP stainless steel stents can be resistant to breakdown at potentials up to over 0.8 V in simulated physiological solutions.[62,64]

Co–Cr alloys. The localized corrosion behavior of Co–Cr alloys is quite different from that of nitinol and stainless

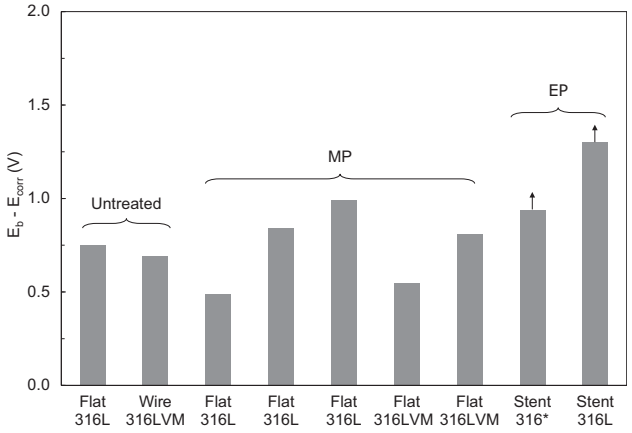

FIGURE 2. Typical values of E_b–E_{corr} for 316L/LVM stainless steel in simulated physiological solutions (PBS and Hanks). Samples are grouped by surface finish. Flat samples include disks, plate, and resin-mounted sections. The asterisk indicates that the specific grade of 316 was not reported. Arrows indicate that the actual values are higher than shown by the bars.

steel. Cyclic polarization tests indicate that Co–Cr alloys in general are not susceptible to pitting corrosion in simulated physiological solutions.[72] Transpassive dissolution can occur with these alloys but only at potentials above 0.6–0.7 V,[72] so it is not expected to be of concern under in vivo conditions.

In vivo environments

The use of in vitro E_b–E_{corr} values to assess the susceptibility to localized corrosion in vivo must take into account the in vivo environment. Various studies have indicated that PBS, Ringer's, and Hanks solutions are satisfactory substitutes for blood and possibly other extracellular body fluids in terms of localized corrosion.[3,27,73,74] Nevertheless, since cyclic polarization tests are performed in simulated physiological solutions under deaerated conditions, it is valuable to have some rationale for using the localized corrosion susceptibility determined from these tests to predict the susceptibility in vivo. In principal, several factors could cause differences in the susceptibility between in vitro and in vivo exposure: organic components, oxygen, and time.

Organic components. Proteins in blood are known to adsorb on the surface of nitinol and 316 stainless steel,[75–77] but they do not appear to negatively impact E_b–E_{corr} values in blood relative to those in simulated physiological solutions. Tests on MP and black oxide (BO) nitinol wire showed that the values of E_b–E_{corr} were higher in bovine serum than in PBS under the same conditions, although the differences were not statistically significant.[73] In addition, Carroll and Kelly found that E_b–E_{corr} for both MP and heat-treated nitinol wire was higher in blood than in Ringer's or 0.9% NaCl solutions, with the qualification that the corrosion behavior in blood was possibly affected by the addition of an anticoagulant containing sodium citrate.[3] Results consistent with these studies were obtained in later work by Lonn et al. on BO and EP-passivated nitinol wire.[78] The values of E_b–E_{corr} in blood were shown to be comparable to or higher than those in PBS, although heparin was added to the blood as an anticoagulant. Heparin is known to undergo competitive adsorption with albumin on Ti[79] and, like citrate, could affect the corrosion behavior of nitinol. Nevertheless, the three studies taken together suggest that E_b–E_{corr} is not adversely affected by proteins and amino acids in blood. Consequently, values of E_b–E_{corr} obtained in simulated physiological solutions should largely be applicable in blood.

Oxygen. Biomedical materials and devices, like metallic materials in general, typically exhibit a shift in E_{corr} to more positive values on exposure to oxygen. As a result, E_b–E_{corr} generally differs in magnitude between deaerated and aerated conditions. In the case of EP nitinol wire, E_{corr} was reported to be about 0.09 V more positive in aerated PBS than in deaerated PBS for exposure times up to 60 h.[80] The corresponding decrease in E_b–E_{corr} ranged from about 0.2 V for a 1-h exposure to less than 0.01 V for a 12-h exposure. These results suggest that an allowance may need to be made in using E_b–E_{corr} values obtained in deaerated test solutions to assess the localized corrosion susceptibility in vivo at shorter exposure times. However, Lonn et al. found that, for a 1-h exposure, the values of E_b–E_{corr} for BO and EP-passivated nitinol wire in deaerated PBS were comparable to those in naturally aerated blood.[78] It is worth noting that an EP nitinol device with an E_b–E_{corr} value of 0.65 V (discussed above) should possess enough of a safety margin in its corrosion resistance to have little likelihood of undergoing localized corrosion in vivo, irrespective of exposure time.

Exposure time. Long-term exposure has been shown to lead to increases in E_b for as-drawn 316LVM wire, as noted above, and for nitinol wire and stents. Clarke et al. found that E_b for various nitinol wire samples gradually increased with time during immersion for up to 6 months.[74] Polarization curves shown for one sample indicate that relatively little change occurred in E_{corr}, so the implication from the resulting E_b–E_{corr} values is that extended exposure in a simulated physiological solution actually increases the resistance to pitting corrosion.

Increases in E_b have also been reported in other work on nitinol wire. Warner found that E_b for BO nitinol wire increased as the immersion time in deaerated PBS was increased from 1 to 66 h.[61] E_{corr} also increased but to a lesser extent, with the result that E_b–E_{corr} also showed an increase, which was consistent with the work of Clarke et al. Nitinol stents made from EP wire and heat-treated in air likewise showed an increase in both E_{corr} and E_b as the immersion time in PBS was increased from 1 to 672 h. In this case, E_b–E_{corr} did not exhibit a statistically-significant increase, but the results showed that even thermally oxidized stents can maintain a steady resistance to pitting corrosion. A similar study found that E_{corr} and E_b for MP and EP nitinol wire increase with immersion time up to 720 h (30 days) in both deaerated and aerated PBS.[80] The combination of increases meant that E_b–E_{corr} did not change significantly in most cases, but the key point again is that the

resistance to pitting corrosion was stable and did not decrease with exposure time.

The more recent work by Lonn et al. involving BO and EP-passivated nitinol wire confirmed the findings of Clarke et al. and Warner that extended exposure tends to increase the resistance to pitting corrosion.[78] Both E_b and E_b–E_{corr} were found to increase when the immersion time was lengthened from 1 to 200 h in a simulated physiological solution (deaerated and aerated PBS) and naturally aerated blood.

GALVANIC CORROSION

Galvanic corrosion tests on medical implants are performed in accordance with ASTM Standard F3044, Standard Test Method for Evaluating the Potential for Galvanic Corrosion for Medical Implants.[81] This standard can be used to assess the effect of coupling between devices such as overlapping stents of different alloys or between parts within a device such as a stent and its markers. The galvanic current (I_{galv}) and potential between the metallic couple are measured in a simulated physiological solution under aerated conditions.

Although the electrolyte is required to be aerated in these tests, aeration can be expected to have little effect generally on I_{corr} in the case of biomedical alloys, because I_{corr} for these passive alloys—uncoupled and coupled—is governed by the anodic reaction, as noted above.[30,82] Such behavior was found to be the case for EP nitinol in PBS.[31] Because the anodic reaction is rate-controlling, the selection of air or a gas mixture with a lower oxygen content for aeration is largely immaterial for most galvanic corrosion tests involving biomedical materials and devices.

I_{galv} represents the increase in I_{corr} produced by coupling between different devices or parts within a device, so it should be compared with I_{corr} for the uncoupled parts or devices. The galvanic effect between parts may be negligible in some devices because of the relative surface area of the parts. Coupling between a stent and noble-metal markers, for example, should have little effect, because the total area of the markers is generally small compared with that of the stent. In addition, part of both I_{corr} and I_{galv} for a device may be associated simply with film growth rather than metal dissolution. In such cases, it can be useful to supplement the electrochemical measurements with solution analyses to determine changes in the concentrations of dissolved metals.

No threshold has been established for assessing the magnitude of I_{galv} for a particular device in terms of any practical consequences. Nevertheless, two points should be considered. First, the question of whether I_{galv} represents a significant increase in I_{corr} depends on the precision of the I_{corr} measurements. Second, as noted above, I_{galv} may partly reflect growth of the surface oxide and not just metal dissolution. For EP or passivated biomedical metals and alloys, oxide growth is likely to be limited and therefore make minimal contribution to I_{galv}, as found for EP nitinol.[31]

Although galvanic coupling is commonly viewed in terms of general corrosion, it can also cause shifts in E_{corr} that result in pitting corrosion, if E_b is exceeded. Such behavior has been observed for MP nitinol coupled with Pt in aerated PBS.[31] EP nitinol, in contrast, did not undergo pitting corrosion and in fact exhibited a relatively small value of I_{galv}.

FRETTING CORROSION

Fretting corrosion is a potential concern with orthopedic implants and small implants such as braded wire stents or overlapped stents. Two ASTM standards describe test methods to evaluate fretting corrosion of orthopedic implants. One of the standards, F897, Standard Test Method for Measuring Fretting Corrosion of Osteosynthesis Plates and Screws, is intended as a screening test for determining the metal loss from osteosynthesis plates and screws.[83] The other standard, F1875, Standard Practice for Fretting Corrosion Testing of Modular Implant Interfaces: Hip Femoral Head-Bore and Cone Taper Interface, provides two methods for the measurement of fretting corrosion at the interfaces of modular hip implants subjected to cyclic loading.[84] The first method incorporates a solution analysis for dissolved metals and a qualitative evaluation of damage and particulate debris. The second method involves an electrochemical evaluation that is intended to provide a qualitative assessment of design changes.

An approach used for stents has been to assess the effect of fretting on their corrosion behavior in two steps. Braided wire stents or overlapped pairs of stents are first subjected to fatigue cycling and then evaluated for their susceptibility to pitting corrosion through cyclic polarization tests under ASTM Standard F2129.[39] Fretting wear can remove the surface oxide and, in the case of an EP or passivated stent, expose inclusions that were not as prevalent or possibly as large as on the treated surface. As noted above, pitting appears to initiate at inclusions in EP nitinol and 316 stainless steel, so greater exposure of inclusions could render the stents more susceptible to pitting corrosion in the areas of wear. For this type of approach to be valid, the type of displacement (radial or axial with or without bending) and the number of fatigue cycles (test duration) must be appropriate to produce fretting representative of that likely to occur in vivo.

Studies of the effect of fretting on the breakdown behavior have produced conflicting results. In one study, it was found that fretting produced by rotating a wire against another wire did not have a significant effect on E_b for MP35N, EP nitinol, or 316LVM stainless steel.[85] In another study, however, fretting produced in axial fatigue tests of overlapped EP nitinol and stainless steel (grade not given) stents resulted in breakdown, whereas non-fatigued stents did not exhibit breakdown up to about 0.9 V.[39] In most cases, pitting on the fatigued stents occurred in the fretting damaged areas. The question of whether axial loading itself played a role has been raised,[85] but other work has shown that nitinol wire subject to 4% tensile strain, resulting in the formation of stress-induced martensite, does not exhibit a substantial change in localized corrosion resistance.[86] Similarly, EP nitinol deformed by bending to 10% strain was found to remain resistant to breakdown up to about 1 V.[67]

SUMMARY

Although electrochemical techniques are widely used to evaluate the corrosion performance of metallic biomedical materials and devices, some questions have been raised about application of the test results to predict the corrosion performance of an implantable device in vivo. Three crucial aspects are (1) the use of simulated physiological solutions to represent actual physiological fluids, (2) the interpretation of test results in terms of how to treat them, and (3) the assessment of test results to determine whether the corrosion performance is acceptable for use of the device in vivo.

Various studies have indicated that the simulated physiological solutions commonly used in electrochemical tests are in fact satisfactory substitutes for blood and other physiological fluids. In the case of blood, the proteins and amino acids do not appear to adversely affect the corrosion rate or the localized corrosion susceptibility. However, some allowance for the effect of oxygen may be necessary in using results obtained in deaerated test solutions to assess the localized corrosion susceptibility in vivo.

Interpretation of test results and assessment of corrosion performance depend on the form of corrosion:

- General corrosion and associated metal ion release can be evaluated in terms of I_{corr}. For surface-treated devices, I_{corr} should closely represent the rate of metal ion release. Although metal ion release is often viewed in relation to normal dietary intake levels, there do not appear to be any broadly accepted limits for metal ion release.
- Pitting corrosion susceptibility is reflected by E_b–E_{corr} rather than by E_b alone. Despite debate in the literature about acceptable values of E_b–E_{corr}, no consensus has been reached on a suitable threshold value for use of an implantable device in vivo.
- Galvanic corrosion is generally evaluated with regard to I_{galv}. Since I_{galv} represents the increase in I_{corr}, the question of whether I_{galv} is significant depends on the magnitude of I_{corr}. Selection of a suitable threshold value for I_{galv} may be difficult, because even a large I_{galv} could have little practical consequence, if I_{corr} were very low.
- Fretting corrosion of some small devices, particularly stents, has been evaluated using E_b–E_{corr} values, but the application of cyclic polarization testing (ASTM F2129) to fatigue-cycled stents has yet to be adopted as a recognized approach for assessing the effect of fretting on the corrosion resistance of stents.

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