Thin Film Options for Implanted Medical Devices

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Background

To realise novel neuroprostheses and neuromodulators, new methods for further miniaturisation of chronically implanted medical devices need to be developed; thin film technology may achieve this. In addition to the requirements of standard thin films, these structures may be continuously exposed to bodily fluids. The operating environment will be wet saline, and highly oxidising species which the body produces in the post-implantation inflammation response will be present [1,2]. The pH may also vary over the range of 5.6 to 9.0 [3]. All of these may combine to promote corrosion and eventually cause device failure. Therefore the implant maker's toolbox is restricted to metals which, within this pH range, are:

(1) immune to corrosion in bodily fluids; or
(2) form protective passivating layers that resist corrosion in bodily fluids; and
(3) are not very toxic.

Of the 4 most commonly used metals for thin film interconnects (Au, Ag, Cu, Al), 3 are excluded in the biological working environment (Al, for inadequate passivation, and Cu & Ag for toxic corrosion products) – thus only gold remains. 12 further metals meet the criteria:

a. 7 "noble" metals which retain their metallic surface (Au, Ir, Pt, Rh, Ru, Pd, Os); and
b. 5 self-passivating metals which form protective oxides (Ti, Ta, Nb, Zr and Cr) [3].

To make a functional device, several metals are likely to be necessary. The noble metals form good electrodes and tracks but often require an underlying adhesion layer to bond to the substrate. Fortunately, several of these passivating metals are used for adhesion layers. Metallic interdiffusion can be a problem in the long term; this can be prevented by use of a third diffusion-barrier layer (e.g. Ti/Pd/Au). The development of novel corrosion resistant metallic stacks is important future work.

An advantage of using Au tracks is that wire- or rivet-bonding can be used [4] for making electrical connection. However, if hermetic seals are required to protect integrated circuits (with Al metallisation), then another bonding method may be superior, such as Au-Sn or Au-Si eutectic [5]. Although these seals should be protected by polymer coating, they may under real conditions be exposed to liquid.

We propose to explore the corrosion of metals alone and in combinations to find the most suitable ways to form circuits and micropackages for future microscale implants. Further use of passivation layers (e.g. SiO_x) or encapsulants (silicone/parylene) may protect against the bare-metal corrosion explored here, and is also being explored.

Element	Z	Type	Resistivity @ 295K (10^{-8} Ωm) [7]	Melting Point (ºC) [8]	Substrate Adhesion (glass/ceramic) [9]	Deposition Method [9]	Coefficient of Thermal Expansion (µm/(m·K)) [10]
Al	13	Poorly-Passivating	2.74	660.32	Adequate (<Ti/Cr)	Evaporation (W/Ta filaments). E-beam not recommended.	23.1
Ti	22	Self-Passivating	43.1	1668	Good	Evaporation (W filament) and e-beam.	8.6
Cr	24	Self-Passivating	12.9	1907	Good	Evaporation (W/Ta filament),	4.9
Cu	29	Corrodes; Toxic	1.7	1084.62	Poor (adhesion required)	Evaporation (W/Ta/Mo filaments/boats).E-beam not recommended.	16.5
Zr	40	Self-Passivating	42.4	1855	?	?	5.7
Nb	41	Self-Passivating	14.5	2477	?	?	7.3
Ru	44	Noble	7.4	2334	?	?	6.4
Rh	45	Noble	4.8	1964	?	?	8.2
Pd	46	Noble	10.5	1554.9	Poor (adhesion required; gold-like)	Evaporation (heavy W helix) or e-beam.	11.8
Ag	47	Corrodes; Toxic	1.61	964.78	?	?	18.9
Ta	73	Self-Passivating	13.1	3017	Good (similar to Ti/Cr)	E-beam only; oxides more volatile than metal.	6.3
Os	76	Noble	9.1	3033	?	?	5.1
Ir	77	Noble	5.1	2446	?	?	6.4
Pt	78	Noble	10.4	1768.4	Poor (adhesion required; gold-like)	Evaporation (W filament) and e-beam.	8.8
Au	79	Noble	2.2	1064.18	Poor (adhesion required)	Evaporation (W/Ta/Mo filaments/boats).E-beam not recommended.	14.2

Table 1 – *Properties for Metals for Thin Film Use*

References:

1. Weisman, S. (1968). Metals for implantation in the human body. *Annals of the New York Academy of Sciences*, *146*(1), 80-95.
2. Patrick, E., et al. (2011). "Corrosion of tungsten microelectrodes used in neural recording applications." Journal of Neuroscience Methods **198**(2): 158-171.
3. Pourbaix, M. (1984). "Electrochemical corrosion of metallic biomaterials." Biomaterials **5**(3): 122-134.
4. Stieglitz, T., et al. (2000). "“Microflex”—A New Assembling Technique for Interconnects." Journal of Intelligent Material Systems and Structures **11**(6): 417-425.
5. Saeedi, E., et al. (2006). "Molten-alloy driven self-assembly for nano and micro scale system integration." Fluid Dynamics and Materials Processing **2**(4): 221-245.
6. Pourbaix, M., *Atlas of Electrochemical Equilibria in Aqueous Solutions*. 1966: Pergamon Press.
7. Kittel, C. et al. (1980). "Thermal Physics", 2nd Ed., W. H. Freeman, 1980.
8. Haynes, William M., ed. (2011). CRC Handbook of Chemistry and Physics (92nd ed.). CRC Press. pp. 4.121–4.123. ISBN 1439855110.
9. Berry, R. W., Hall, P. M., & Harris, M. T. (1968). Thin film technology. D. VAN NOSTRAND CO., INC., PRINCETON, N. J. 1968, 706 P.
10. David R. L. (2003), CRC Handbook of Chemistry and Physics, 84th Edition. CRC Press. Boca Raton, Florida.

Pourbaix (pH/potential) Diagrams & Corrosion Analysis

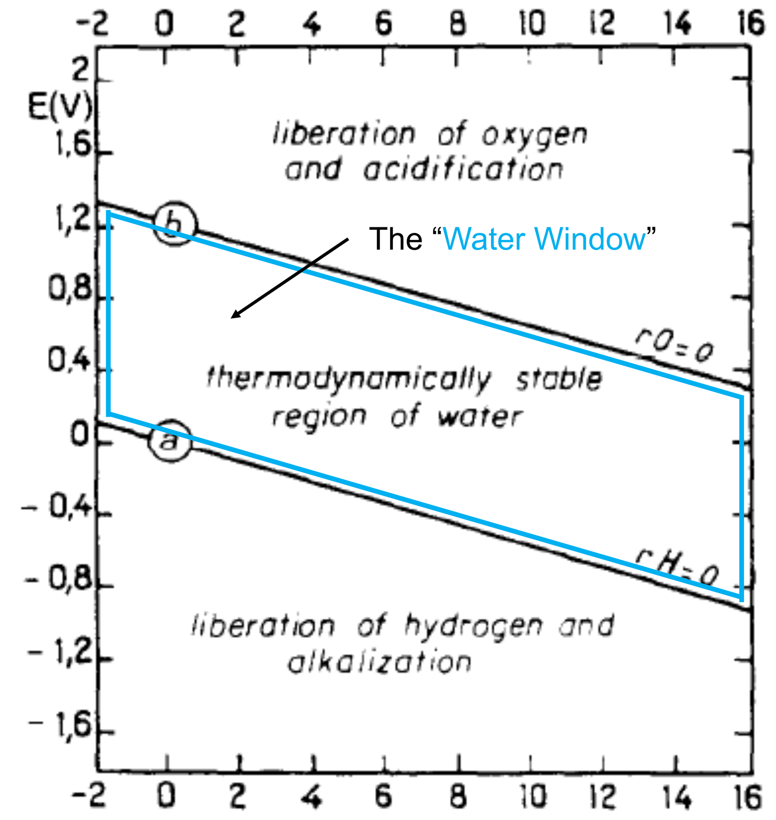
Pourbaix diagrams are a powerful tool for predicting the corrosion behaviour of metals in aqueous solutions. Implanted medical devices have electrodes that may record electrical potentials or stimulate the nervous system by applied charge, and the behaviour of metals at these potentials may be predicted. All implants must operate safely, and thus will remain within the "water window"; evolution of gases via the electrolysis of water will cause unacceptable tissue damage.

Limitations:

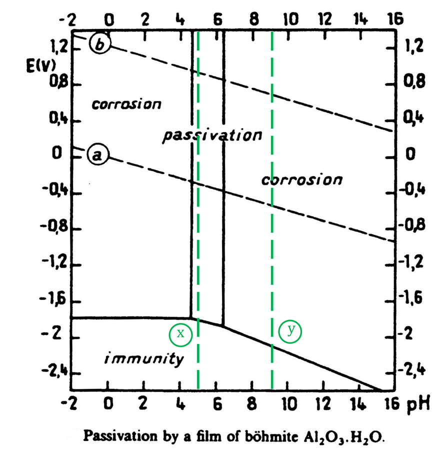
- Does not inform of the kinetics of potential corrosion reactions, but only the thermodynamics
- Diagrams are constructed under strict experimental conditions, which may not reflect accurately the operating environment of a chronic implant (e.g. oxidising agents, chlorides).

Legend (for all following diagrams)

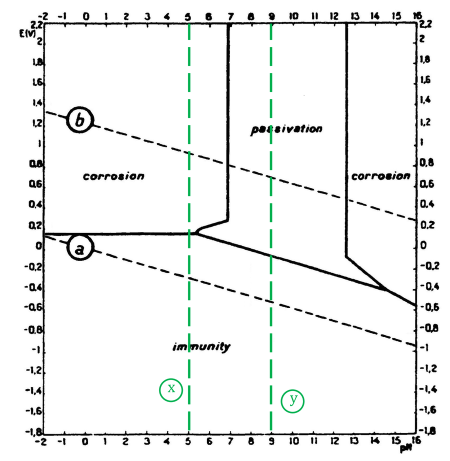
(a) The **oxygen line**, potentials above which water may be <u>oxidised</u> and oxygen evolved.
(b) The **hydrogen line**, potentials below which water may be <u>reduced</u> and hydrogen evolved.
(x) The **pH 5 line**, a safe minimum physiological pH (excluding the gastric environment).
(y) The **pH 9 line**, a safe maximum physiological pH.



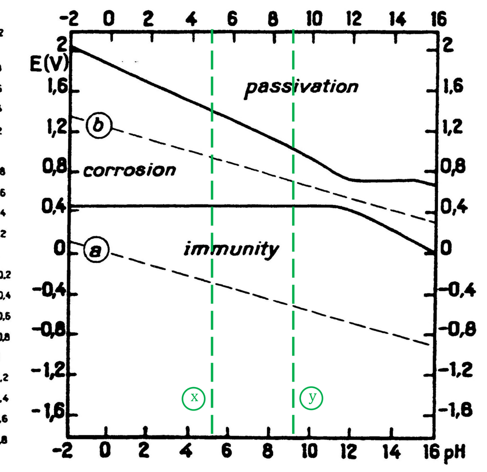
1. Commonly Used Metals for Thin Film Interconnects [6]



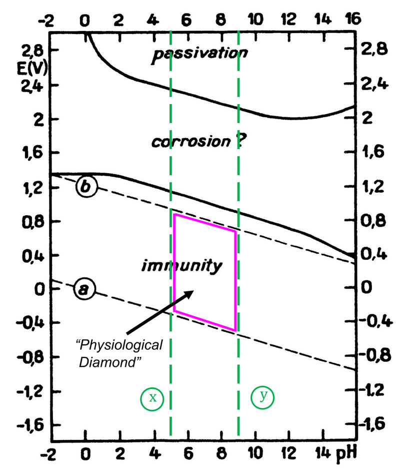
Aluminium ✗



Copper ✗



Silver ✗

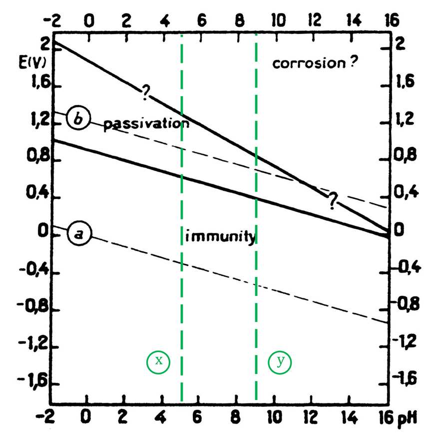


Gold ✓

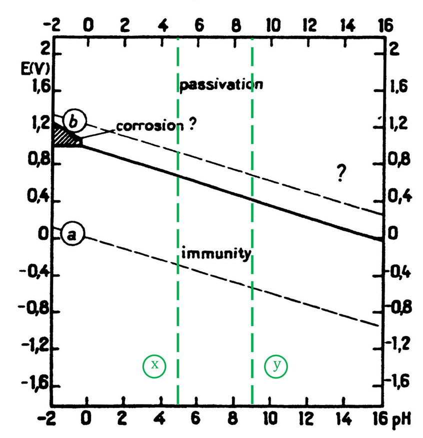
We are interested in the area of the Pourbaix Diagram contained within the *water window* and within the body's *pH window* – the "physiological diamond". Al, Cu & Ag have corroding portions within their physiological diamonds, while Au is fully immune.

Take this corrosion analysis as a very conservative case: bare metal unencapsulated within in physiological solution.

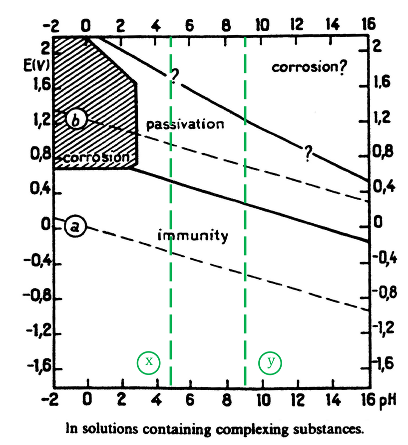
2. Noble Metals (potential vs. pH equilibrium diagram at 25ºC) [6]



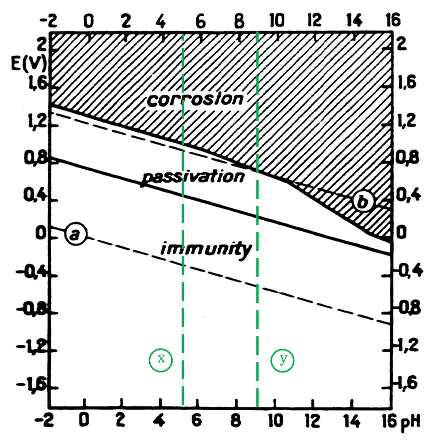
Iridium ✓



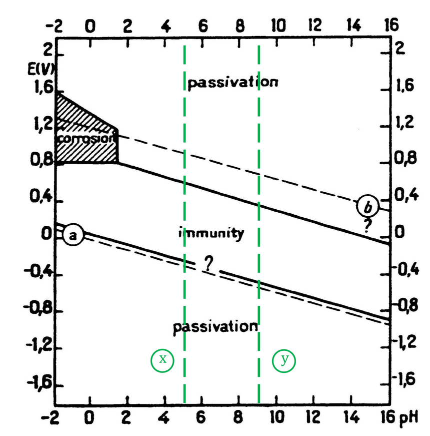
Platinum ✓



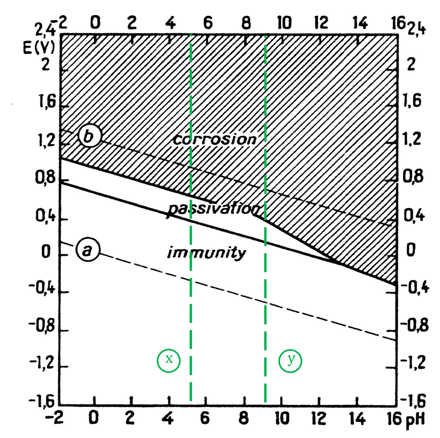
Rhodium ✓



Ruthenium ✓

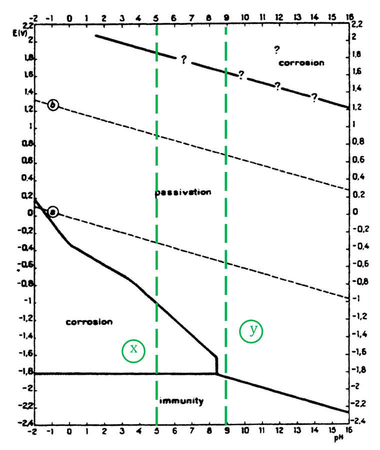


Palladium ✓

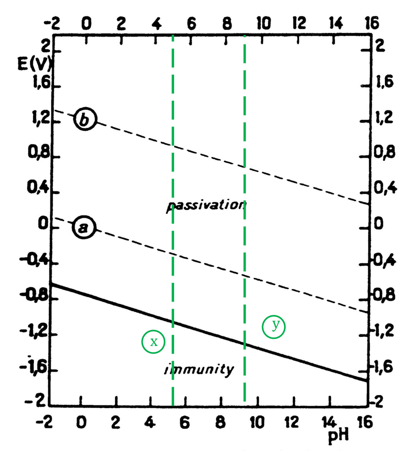


Osmium ?

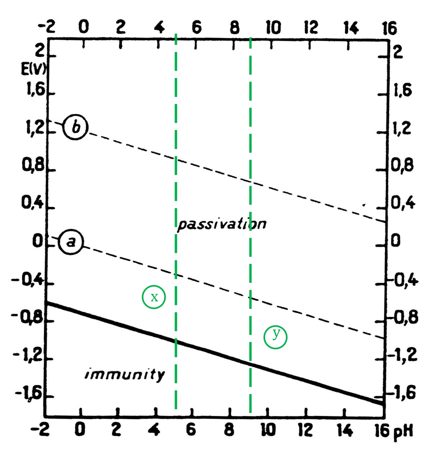
3. Self-Passivating Metals (potential vs. pH equilibrium diagram at 25ºC) [6]



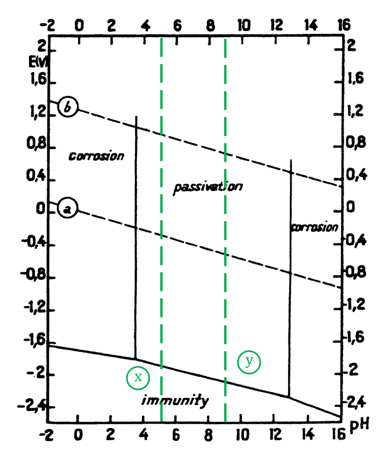
Titanium ✓



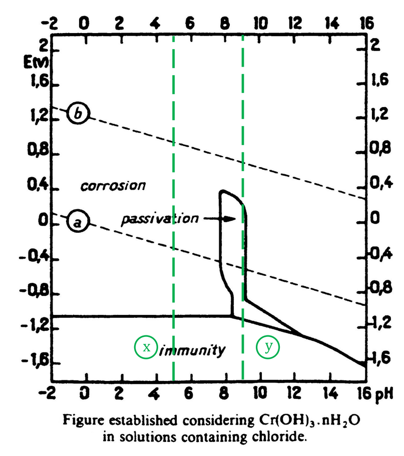
Tantalum ✓



Niobium ✓



Zirconium ✓



Chromium ✗

While it is a common adhesion layer for Au/Pt thin films, the corrosion behaviour of Cr in chloride-rich solutions makes it unsuitable for chronic implant use.