François Cardarelli

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Miscellaneous Electrical Materials

9.1 Thermocouple Materials

9.1.1 The Seebeck Effect

In 1821, Estonian physicist Thomas Johann Seebeck observed that when two wires of dissimilar conductors A and B (i.e., metals, alloys, or semiconductors) are joined together at both ends and the two junctions are kept at two different temperatures, i.e., cold junction temperature T_c and hot junction temperature T_h (Figure 9.1), the temperature differential $\Delta T = (T_h - T_c)$ produces an electric current that flows continuously through the circuit. This phenomenon was called the ***Seebeck effect*** after its discoverer.

When the circuit is open, there appears an electric potential difference called the ***Seebeck electromotive force***, denoted *emf* or e_{AB} and expressed in V. This voltage is a complex function of both the temperature difference and the type of conductors [i.e., $e_{AB} = F(\Delta T, \mathrm{A}, \mathrm{B})$]. In practice, the Seebeck electromotive force is related to the temperature difference by a polynomial equation, where the polynomial coefficients (i.e., c_0, c_1, c_2, c_3, etc.) are empirical constants determined by experiment and that characterize the thermocouple selected.

$$emf = e_{AB} = c_0 + c_1 \cdot \Delta T + c_2 \cdot \Delta T^2 + c_3 \cdot \Delta T^3 + c_4 \cdot \Delta T^4 + \cdots$$

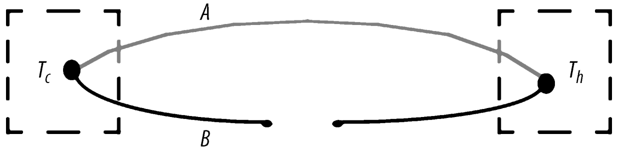

Figure 9.1. Thermocouple basic circuit

Table 9.1. Thermoelectric power Q_{AB} of selected elements and commercial alloys (A) versus pure platinum (B = Pt) for a ΔT = 100°C (in mV vs. Pt)

A	Q_{AB}	A	Q_{AB}	A	Q_{AB}	A	Q_{AB}	A	Q_{AB}	A	Q_{AB}	A	Q_{AB}
Li	+1.82	Be	n.a.	Al	+0.39	C	+0.22	As		Se		Ru	
Na	−0.20	Mg	+0.42	Ga		Si	+44.8	Sb	+4.89	Te	+50.0	Rh	+0.65
K	−0.83	Ca	−0.51	In	+0.69	Ge	+33.9	Bi	−7.34	Cr		Pd	−0.47
Rb	+0.46	Sr	n.a.	Tl	+0.58	Sn	+0.42	V		Mo	+1.45	Os	
Cs	+0.50	Ba	n.a.	Sc		Pb	+0.44	Nb		W	+0.80	Ir	+0.66
Cu	+0.75	Zn	+0.76	Y		Ti	n.a.	Ta	+0.41	Fe	+1.98	Pt	0.00
Ag	+0.73	Cd	+0.91	La		Zr	+1.17	Mn	+0.70	Ni	−1.48	U	
Au	+0.70	Hg	+0.06	Ce	+1.14	Hf	n.a.	Re		Co	−1.33	Th	−0.13

Commercial alloys (mV vs. Pt): Beryllium-copper (97.3Cu-2.7Be): +0.67; yellow brass (70Cu-30Zn): +0.60; nickel-chrome (80Ni-20Cr): +1.14; stainless steel (Fe-18Cr-8Ni): +0.44; lead solder (50Sn-50Pb): +0.46; phosphor bronze (96Cu-3.5Sn-0.3P): +0.55; manganin (84Cu-12Mn-4Ni): +0.61; constantan (45Ni-55Cu): −3.51; Alumel (95Ni-2Mn-2Al): −1.29; Chromel (90Ni-9Cr): +2.81.

However for a small temperature difference, the Seebeck electromotive force can be assumed to be directly proportional to the temperature difference:

$$e_{AB} = \Delta\alpha \cdot \Delta T = \Delta\alpha \cdot (T_h - T_c),$$

where the algebraic physical quantity $\Delta\alpha$ is called the ***relative Seebeck coefficient*** or the ***thermoelectric power***, denoted Q_{AB} and expressed in $V.K^{-1}$. Thermoelectric power corresponds to the difference between the ***absolute Seebeck coefficients*** of the conductors:

$$\Delta\alpha = Q_{AB} = \alpha_A - \alpha_B.$$

In practice, the thermoelectric power of a conductor A is usually reported for a temperature difference of 100°C between hot and cold junction and by fixing the second material B. The second material used as the standard is most of the time pure platinum and, less frequently, copper or even lead. Hence, the thermoelectric power is reported in modern tables in mV versus Pt or mV versus Cu, respectively. Therefore to convert a thermoelectric power measured with a given scale into another scale, the following simple equation can be used:

$$Q_{APt} = Q_{ACu} + Q_{CuPt} \quad \text{with } Q_{CuPt} = +\,0.75 \text{ mV vs. Pt } (0\text{–}100°\text{C}),$$

$$Q_{APt} = Q_{APb} + Q_{PbPt} \quad \text{with } Q_{PbPt} = +\,0.44 \text{ mV vs. Pt } (0\text{–}100°\text{C}).$$

The order of magnitude for thermoelectric power is commonly in the range of several mV/K for semiconductors and of several μV/K for most metals and alloys (Table 9.1). On the other hand, for semiconductors, the theoretical thermoelectric power can be assessed using the following equation, where N_e is the electronic density in the conductor and C_v the molar heat capacity at constant volume:

$$Q_{AB} = -C_v/3eN_e.$$

9.1.2 Thermocouple

A thermocouple is a particular temperature-sensing device consisting, in its simplest design, of two wires made of two dissimilar conductors, A and B, that are joined by two junctions. The cold junction is maintained at a well-known temperature, for instance, the ice point,

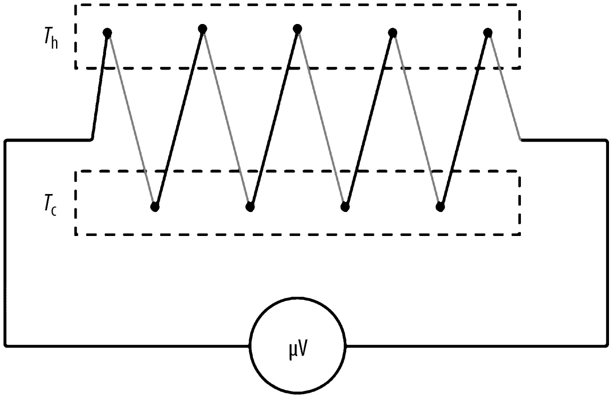

Figure 9.2. Thermocouples in series

while the other junction serves as probe. The electromotive force measured with a high-precision voltmeter is then proportional to the temperature of the hot junction. The signal can even be amplified by connecting in series *n* identical thermocouples (Figure 9.2).

The resulting overall electromotive force ΔV is the sum of all the individual *emf* of each thermocouple and is easier to measure with accuracy:

$$\Delta V = Q_{AB} \cdot \Delta T + Q_{AB} \cdot \Delta T_2 + Q_{AB} \cdot \Delta T_3 + Q_{AB} \cdot \Delta T_4 + \cdots + Q_{AB} \cdot \Delta T_n = Q_{AB} \cdot \textstyle\sum_k \Delta T_k .$$

9.1.3 Properties of Common Thermocouple Materials

Table 9.2. Standard thermocouple types and common uses

Type	Description
Type J	Suitable in reducing, vacuum, or inert atmospheres but limited use in oxidizing atmosphere at high temperature. Not recommended for low temperatures.
Type K	Clean and oxidizing atmospheres, limited use in vacuum or reducing atmospheres. Wide temperature range.
Type S	Oxidizing or inert atmospheres. Beware of contamination. For high temperatures.
Type R	Oxidizing or inert atmospheres. Beware of contamination. For high temperatures.
Type N	More stable than type K at high temperature.
Type B	Oxidizing or inert atmospheres. Beware of contamination. For high temperatures.
Type E	Oxidizing or inert atmospheres, limited use in vacuum or reducing atmospheres. Highest thermoelectric power.
Type C	Suitable in reducing, vacuum, or inert atmospheres. Beware of embrittlement. Not suitable for oxidizing atmospheres and not practical below 400°C.
Type T	Suitable in mid-oxidizing, reducing, vacuum, or inert atmospheres. Good for cryogenic applications.

Table 9.3. Physical properties of selected thermocouple materials

Thermocouple type (ANSI)	Metal and alloy trade names	Average chemical composition (%wt.)	Junction polarity	Density (/kg.m^{-3})	Yield strength 0.2% proof (σ_{YS}/MPa) (annealed)	Ultimate tensile strength (σ_{UTS}/MPa) (annealed)	Elongation (Z/%)	Temperature range (/°C)	Thermoelectric power (/μV.K^{-1})	Melting range (°C)	Coefficient linear thermal expansion (α/10^{-6}K^{-1})	Specific heat capacity (c_P/J.kg^{-1}.K^{-1})	Thermal conductivity (k/W.m^{-1}.K^{-1})	Electrical resistivity (ρ/μΩ.cm)	Temperature coefficient of resistance (0–100°C)
Type J	Iron	Fe	JP	7860	n.a.	234	40	0 to 760	50.2 (0°C)	1539	11.7	447.7	67.78	9.67	0.0065
	Constantan®	45Ni-55Cu	JN	8890	n.a.	552	32			1270	14.9	397.5	22.18	48.9	0.00002
Type K	Chromel®	90Ni-9Cr	KP	8730	n.a.	655	27	–270 to 1372	39.4 (0°C)	1350	13.1	447.7	19.25	70	0.0032
	Alumel®	95Ni-2Mn-2Al	KN	8600	n.a.	586	32			1400	12.0	523	29.71	32	0.00188
Type N	Nicrosil®	84.3Ni-14Cr-1.4Si-0.1Mg	NP	8520	415	760	30	–270 to 1260	26.2 (0°C)	1410	13.3	15.06	130	93	0.00011
	Nisil®	95.5Ni-4.4Si-0.1Mg	NN	8700	380	655	35			1400	12.1	26.61	230	37	0.00078
Type T	Copper OFHC	Cu (99.9%wt,)	TP	8930	69	221	46	–200 to 370	38 (0°C)	1083	16.6	384.9	376.8	1.74	0.0043
	Constantan®	45Ni-55Cu	TN	8890	n.a.	552	32			1270	14.9	397.5	22.18	48.9	0.00002
Type E	Tophel®	90Ni-10Cr	EP	8730	n.a.	670		–200 to 870	58.5 (0°C)	1430	13.1	447.7	19.25	70	0.00032
	Constantan®	45Ni-54Cu-1Mn	EN	8890	450	552	32			1270	14.9	397.5	22.18	48.9	0.00002
Type R	Platinum-13 rhodium	87Pt-13Rh	RP	19,550	190	331	32	–50 to 1768	11.5 (600°C)	1860	9.0	n.a.	36.81	19.6	0.0016
	Platinum	Pt	RN	21,450	70	166	38			1769	9.1	133.9	71.54	10.4	0.00393
Type S	Platinum-10 rhodium	90Pt-10Rh	SP	19,950	180	317	32	–50 to 1768	10.3 (600°C)	1830	10.0	n.a.	37.66	18.9	0.0017
	Platinum	Pt	SN	21,450	70	166	38			1769	9.1	133.9	71.54	10.4	0.00393
Type B	Platinum-30 rhodium	70Pt-30Rh	BN	17,520	n.a.	510	26	800 to 1820	6.0 (600°C)	1910	n.a.	n.a.	n.a.	19.0	0.0020
	Platinum-6 rhodium	94Pt-6Rh	BP	20,510	n.a.	255	34			1810	n.a.	n.a.	n.a.	17.5	0.0014
Alloy 19/20	Alloy 19®	Ni-1Co	P	8900	170	415	35	0 to 1260	n.a.	1450	13.6	n.a.	50	8	n.a.
	Alloy 20®	Ni-18Mo	N	9100	515	895	35			1425	11.9	n.a.	15	165	n.a.
Pt-Mo	Platinum-5 molybdenum	Pt-5Mo	P					1100 to 1500	29	1788					
	Platinum-molybdenum	Pt-0.1Mo	N							1770					

Platinel I	Palladium alloy	83Pd-14Pt-3Au	P						41.9	1580					
	Gold-palladium	65Au-35Pd	N							1426					
Platinel II	Palladium alloy	55Pd-31Pt-14Au	P						42.4	1500					
	Gold-palladium	65Au-35Pd	N							1426					
W-Re	Tungsten	W	P	19,900		552	3	0 to 2760	16.7	3410					0.0048
	Tungsten-rhenium	W-26Re	N	19,700		1517	10			3120					
W-Re	Tungsten-rhenium	W-3Re	P	19,400		1241	10	0 to 2760	17.1	3360				9.14	0.0003
	Tungsten-rhenium	W-25Re	N	19,700		1448	10			3130				27.43	0.0012
Type C	Tungsten-rhenium	W-5Re	P	19,400		1379	10	0 to 2760	19.5 (600°C)	3350				11.63	n.a.
	Tungsten-rhenium	W-26Re	N	19,700		1517	10			3120				28.3	n.a.

Table 9.4. NIST polynomial equations for thermocouples

Thermocouple type	Polynomial equation with NIST coefficients and electromotive force in volts
Type E	$T_E(°\mathrm{C}) = +0.104967248 + 17{,}189.45282\,\Delta E - 282{,}639.0850\,\Delta E^2 + 1.26953395 \times 10^7\,\Delta E^3 - 4.487030846 \times 10^8\,\Delta E^4 + 1.10866 \times 10^{10}\,\Delta E^5 - 1.76807 \times 10^{11}\,\Delta E^6 + 1.71842 \times 10^{12}\,\Delta E^7 - 9.19278 \times 10^{12}\,\Delta E^8 + 2.06132 \times 10^{13}\,\Delta E^9$
Type J	$T_J(°\mathrm{C}) = -0.048868252 + 1.987314503 \times 10^4\,\Delta E - 2.186145353 \times 10^5\,\Delta E^2 + 1.156919978 \times 10^7\,\Delta E^3 - 2.649175314 \times 10^8\,\Delta E^4 + 2.018441314 \times 10^8\,\Delta E^5$
Type K	$T_K(°\mathrm{C}) = +0.226584602 + 2.4152109 \times 10^4\,\Delta E + 6.72334248 \times 10^4\,\Delta E^2 + 2.210340682 \times 10^6\,\Delta E^3 - 8.609639149 \times 10^8\,\Delta E^4 + 4.83506 \times 10^{10}\,\Delta E^5 - 1.18452 \times 10^{12}\,\Delta E^6 + 1.38690 \times 10^{13}\,\Delta E^7 - 6.33708 \times 10^{13}\,\Delta E^8$
Type R	$T_R(°\mathrm{C}) = +0.263632917 + 1.79075491 \times 10^5\,\Delta E - 4.884034137 \times 10^7\,\Delta E^2 + 1.90002 \times 10^{10}\,\Delta E^3 - 4.82704 \times 10^{12}\,\Delta E^4 + 7.62091 \times 10^{14}\,\Delta E^5 - 7.20026 \times 10^{16}\,\Delta E^6 + 3.71496 \times 10^{18}\,\Delta E^7 - 8.03104 \times 10^{19}\,\Delta E^8$
Type S	$T_S(°\mathrm{C}) = +\,0.927763167 + 1.69526515 \times 10^5\,\Delta E - 3.156836394 \times 10^9\,\Delta E^2 + 8.990730663 \times 10^9\,\Delta E^3 - 1.63565 \times 10^{12}\,\Delta E^4 + 1.88027 \times 10^{14}\,\Delta E^5 - 1.37241 \times 10^{16}\,\Delta E^6 + 6.17501 \times 10^{17}\,\Delta E^7 - 1.56105 \times 10^{19}\,\Delta E^8 + 1.69535 \times 10^{20}\,\Delta E^9$
Type T	$T_T(°\mathrm{C}) = +\,0.10086091 + 2.572794369 \times 10^4\Delta E - 7.673458295 \times 10^5\,\Delta E^2 + 7.802559581 \times 10^7\,\Delta E^3 - 9.247486589 \times 10^9\,\Delta E^4 + 6.97688 \times 10^{11}\,\Delta E^5 - 2.66192 \times 10^{13}\,\Delta E^6 + 3.94078 \times 10^{14}\,\Delta E^7$

9.2 Resistors and Thermistors

Resistors are special conductive metals and alloys, such as manganin, each having an accurate and well-known electrical resistivity combined with an extremely low temperature coefficient, and for that reason they are currently used in high-precision electric and electronic instruments and devices like calibrated resistances, shunts, and rheostats. Two major classes must be distinguished depending on their end use:

(i) ***Resistance alloys*** are special conductive metals and alloys having a uniform and stable electrical resistivity combined with a constant temperature coefficient and a low thermoelectric power versus copper; manganin and pure platinum are well-known examples.

(ii) ***Heating alloys*** are metals or alloys having a high electrical resistivity combined with a high melting point; hence they are selected as heating elements in resistance furnaces; nickel-chromium is a typical example.

9.2.1 Electrical Resistivity

Electrical resistivity is an intrinsic property of a resistor material that allows for the calculation of the electrical resistance, R, expressed in Ω, of a homogeneous conductor with a regular cross-sectional area, A, expressed in square meters, and a length, L in meters. R is given by the following equation, where the proportional quantity, ρ, is the electrical resistivity of the material, expressed in Ω.m:

$$R = \rho(L/A).$$

9.2.2 Temperature Coefficient of Electrical Resistivity

Over a narrow range of temperatures, the electrical resistivity, ρ, varies linearly with temperature according to the equation below, where α is the ***temperature coefficient*** of the electrical resistivity expressed in $\Omega.\text{m}.\text{K}^{-1}$:

$$\rho(T) = \rho(T_0)\,[1 + \alpha(T - T_0)].$$

The temperature coefficient of electrical resistivity is an algebraic physical quantity (i.e., negative for semiconductors and positive for metals and alloys) defined as follows:

$$\alpha = 1/\rho_0(\partial\rho/\partial T).$$

It is important to note that in theory the temperature coefficient of electrical resistivity is different from that of the electrical resistance denoted a and defined as follows:

$$R(T) = R(T_0)\,[1 + a\,(T - T_0)],$$

with $a = 1/R_0(\partial R/\partial T)$.

Actually, electric resistance, as defined in the previous paragraph, also involves the length and the cross-sectional area of the conductor, so the dimensional change of the conductor due to temperature change must also be taken into account. We know that both dimensional quantities vary with temperature according to their coefficient of linear thermal expansion (α_L) and the coefficient of surface thermal expansion (α_S), respectively, in addition to that of electrical resistivity. Hence the exact equation giving the variation of the resistance with temperature is given by:

$$R = \rho_0\,[1 + \alpha(T - T_0)]\{L_0\,[1 + \alpha_L\,(T - T_0)]\}/\{A_0\,[1 + \alpha_S\,(T - T_0)]\}.$$

Table 9.5. Resistors used in electrical and electronic devices (shunts and rheostats)

Resistor material (composition)	Density (ρ/kg.m^{-3})	Yield strength (σ_{YS}/MPa)	Ultimate tensile strength (σ_{UTS}/MPa)	Elongation (Z/%)	Thermal conductivity (k/Wm^{-1}K^{-1})	Specific heat capacity (c_p/Jkg^{-1}K^{-1})	Coefficient of linear thermal exp. up to 1000°C (a/10^{-6}K^{-1})	Electrical resistivity (ρ/μΩ.cm)	Temperature coeff. electrical resistivity (0–100°C) (a/10^{-6} K^{-1})	Maximum operating temperature (T/°C)	Major uses
Alkrothal® 14 (93.8Fe-15Cr-0.7Si-0.5Mn)	7280	445–455	600–630	22	16	460	15	125		1100	Electrical resistance wire for low-temperature applications
Constantan® (45Ni-54Cu-1Mn)	8890	450	552	32		410	19.5	48.9	–20	600	Wire-wound precision resistors, potentiometers, volume-control devices, winding heavy-duty industrial rheostats, and electric motor resistances
Kanthal® 52 (52Ni-48Fe)	8200	340	610	30	17	500	10	37	+3300		Low-resistivity material with a high temperature coefficient of resistance used in voltage regulators, timing devices, temperature-sensitive resistors, temperature-compensating devices, and low-temperature heating applications
Kanthal® 70 (70Ni-30Fe)	8450	340	640	30	17	520	15	21	+3500	600	
Manganin® (84Cu-12Mn-4Ni)	8410	275	620		20		18.7	48.2	+15		Material with low coefficient of resistance used in shunts
Manganin-shunt® (86Cu-10Mn-4Ni)	8420	345	690				18.7	38	+10		
MnLow	8410		420–690	25				43			Precision electrical measuring apparatus and resistors
Nichrome® 80-20	8300	300–420	725–810	30	15	460	18	109	+50	1100	Heaters
Resistor Alloy 30	8900	290	640	25				30		400	General resistance wires, cores of low-temperature heaters, resistance elements of heaters for electrical circuit breakers/fuses
Resistor Alloy 15	8900	340	690	25				15		400	
Resistor Alloy 10	8900	230	680	25				10		400	
Resistor Alloy 5	8900	220	440	25				5		400	

Table 9.6. Resistors used in electric furnaces

Class	resistor material (composition)	Density (ρ/kg.m^{-3})	Yield strength (σ_{YS}/MPa)	Ultimate tensile strength (σ_{UTS}/MPa)	Elongation (Z/%)	Thermal conductivity (k/Wm^{-1}K^{-1})	Specific heat capacity (c_p/Jkg^{-1}K^{-1})	Coeffi. linear thermal exp. up to 1000°C (a/10^{-6}K^{-1})	Electrical resistivity (ρ/μΩ.cm)	Temperature coefficient of electrical resistivity (0–100°C) (α/10^{-5}K^{-1})	Melting point (°C)	Maximum operating temperature (T/°C)	Applications
Medium temperature (up to 1400°C)	Nichrome 35-20 (42Fe-35Ni-20Cr-2Si-1Mn)	7900	450	750	30	13	500	19	104	230	1390	1000	Industrial furnaces, heating elements of cooking equipment
	Nichrome 40-20 (40Ni-38Fe-20Cr-1Mn-1Si)	7900	300–450	650–750	30	13	500	19	96–105	230	1390	1050	Domestic heating appliances, industrial furnaces (carburizing or semireducing atmosphere)
	Nichrome 60-15 (60Ni-20Fe-18Cr-1Mn-1Si)	8200	300–370	700–730	30–35	13	480	17	112	110	1390	1150	Industrial furnaces, electrically heated equipment, high-resistance and potentiometer resistors
	Nichrome 80-20 (78Ni-20Cr-1Fe-1Si)	8300	300–420	725–810	30	15	460	18	109	50	1400	1200	Industrial furnaces, electric cooking equipment, precision resistors (oxidizing, reducing, vacuum)
	Nichrome 70-30 (68Ni-30Cr-1Mn-1Si)	8100	425–430	800–820	30	14	460	17	118	50	1380	1250	Industrial furnaces, precision resistors
	Kanthal® AE (Fe-22Cr-5.3Al-0.7Si-0.4Mn-0.08C)	7150	520	720	20	11	460	15	139	60	1500	1300	Heating elements for ceramic glass top hobs and quartz tube heaters
	Kanthal® AF (Fe-22Cr-5.3Al-0.7Si-0.4Mn-0.08C)	7150	475–500	680–700	18–23	11	460	15	139	60	1500	1300	Heating elements in industrial furnaces and in electrical appliances
	Kanthal® A (Fe-22Cr-5.3Al-0.7Si-0.08C)	7150	550	725	22		460	15	139	60	1500	1350	

Medium temperature (up to 1400°C)	Kanthal® A-1 (Fe-22Cr-5.8Al-0.7Si-0.08C)	7100	475–545	680–780	18–20	26	460	15	145	40	1500	1400	High-temperature furnaces for heat treatment and firing of ceramics, oxidizing and carburizing atmospheres
	Kanthal® APM (Fe-22Cr-5.8Al-0.7Si-0.4Mn-0.08C)	7100	470	680	20	26	460	16	145	40	1500	1425	High-temperature furnaces in electronics industries and in diffusion furnaces
High temperature (up to 1700°C)	Silicon carbide (SiC)	3200		28				4.7	99–199		2410	1650	Oxidizing atmosphere
	Platinum (Pt)	21,450				71.6	132	9.1	9.81	+3920	1772	1600	Oxidizing, reducing, vacuum
Super high temperature (1900–3000°C)	Molybdenum disilicide ($MoSi_2$)	6240		185				9.2–13.1	27–37		2050	1950	Oxidizing atmosphere to maintain protective silica layer
	Ziconia stabilized (ZrO_2-8 mol% Y_2O_3)											1500–2000	Secondary resisting coil requires a preheater to reach 800°C
	Molybdenum (Mo)	10,220				142	251	5.43	5.2	+4350	2621	2000	
	Tantalum (Ta)	16,654				58	140	6.6	12.45	+3820	2996	2300	
	Graphite (C)	1600		1.8		350	709	1.3	910		3650	3000	
	Tungsten (W)	19,300				71	136	4.59	5.65	+4800	3413	3000	Reducing, vacuum

Table 9.7. Upper temperature limits in degrees Celsius for selected high-temperature resistors in various furnace atmospheres

High-temperature resistor	Ar	CO	He	N_2	CO_2	NH_3	CH_4	H_2
Graphite	3000	3000	3000	2200	900	2200	3000	2700
Molybdenum	1650	1400	1650	1650	1200	2200	1100	1650
Tantalum	2800	1000	2800	2000	1250	400	900	1000
Tungsten	3000	800	3000	2300	1200	3000	900	3000

However, in most practical cases, the two coefficients of thermal expansion are generally much smaller than the temperature coefficient of electrical resistivity. Therefore, if dimensional variations are negligible, values of the coefficient of electrical resistivity and that of electrical resistance can be assumed to be identical.

Sometimes, in practice, electrical engineers use another dimensionless physical quantity to characterize the variations of the electrical resistivity between room temperature and a given operating temperature T, which is simply termed the coefficient of temperature, denoted C_T and defined as a dimensionless ratio:

$$C_T = \rho(\mathrm{T})/\rho(T_0).$$

Therefore the relationship existing between the temperature coefficient of electrical resistivity and the coefficient of temperature is as given below:

$$\alpha = [(C_T - 1)/(T - T_0)].$$

Example: For pure platinum metal ($\alpha = 0.00392\ \mathrm{K}^{-1}$), which is used extensively in high-precision devices for accurate temperature measurement called ***resistance temperature detectors*** (RTD), the coefficient of temperature for the resistance of 100 ohms between the freezing point (0°C) and the boiling point of water (100°C) is $a = 0.00385\ \mathrm{K}^{-1}$ [RTD of Class B according to standard IEC-751].

See Tables 9.5–9.7, pages 549–551.

9.3 Electron-emitting Materials

To extract an electron from an atom with a kinetic energy K, an **ionizing energy** E (i.e., thermal, mechanical, chemical, electrical, or optical) is required that is superior to the **binding energy** of the electron, B. The kinetic energy released to the ionized electron is given by the equation $K = E - B$. In a solid, electron extraction implies the provision of electrons with sufficient energy to reach the difference between the Fermi level (i.e., the electrochemical potential of an electron inside the solid crystal lattice) and the surface potential energy at vacuum level and absolute zero. This energy difference is called the ***electron work function***, denoted W_S, and it is expressed in Joules (eV). The thermal emission of electrons, ***thermoelectronic*** or ***thermoionic emission***, is characterized by electrons leaving the surface of a material because of thermal activation. Actually, electrons having sufficient kinetic energy on account of their thermal motion escape from the material surface so increasing the temperature at the surface of a material will increase the flow of electrons (i.e., electric current). The electric current density, expressed in $\mathrm{A.m^{-2}}$, as a function of the absolute temperature of the material surface is given by the ***Richardson–Dushman*** equation as follows:

$$J_S = AT^2(1 - r)\exp[-W_S/kT],$$

where A is the ***Richardson constant*** expressed in $\mathrm{A.m^{-2}K^{-2}}$ and r is the dimensionless reflection coefficient of the surface for zero applied electric field (i.e., usually negligible). In theory, the Richardson constant would be equal to 1.2 $\mathrm{MA.m^{-2}K^{-2}}$, but in practice, because the work function is also a function of temperature, A varies over a wide range of magnitude. The theoretical value of A is given in quantum theory and described below:

$$A = 4\pi mk^2e/h^3.$$

Electron-emitting materials (commonly referred to as thermoionic emitters) can be classified as pure-metal emitters (e.g., W, Ta), monolayer-type emitters, oxide emitters, chemical-compound emitters, and finally alloy emitters. Thermoionic properties of selected materials are listed in Table 9.8.

Table 9.8. Thermoionic properties of selected materials

Material	Electron work function (W_S/eV)	Richardson constant (A/kA.m^{-2}.K^{-1})	Material	Electron work function (W_S/eV)	Richardson constant (A/kA.m^{-2}.K^{-1})
Ferrous metals			**Refractory carbides**		
Iron (ferrite)	4.5	260	Carbon	5.0	150
Cobalt	5.0	410	TaC	3.14	3
Nickel	4.61	300	TiC	3.35	250
Common nonferrous			ZrC	2.18	3
Copper	4.65	1200	SiC	3.5	640
Other metals			ThC_2	3.5	5500
Beryllium	4.98	3000	Refractory borides		
Barium	2.52	600	CeB_6	2.6	36
Caesium	2.14	1600	LaB_6	2.7	290
Platinum group metals (PGMs)			ThB_6	2.9	5
Osmium	5.93	1,100,000	CaB_6	2.9	26
Rhodium	4.98	330	BaB_6	3.5	160
Iridium	5.27	1200	Refractory oxides		
Platinum	5.65	320	ThO_2	2.6	50
Refractory metals (groups IVB, VB, and VIB)			CeO_2	2.3	10
Titanium	4.53	n.a.	La_2O_3	2.5	9
Zirconium	4.05	3300	Y_2O_3	2.4	10
Hafnium	3.60	220	BaO-SrO	1.0	10
Niobium	4.19	1200	Uranides		
Tantalum	4.25	1200	Uranium	3.27	60
Molybdenum	4.15	550	Thorium	3.38	700
Tungsten	4.55	600			

9.4 Photocathode Materials

When a monochromatic electromagnetic radiation with a frequency ν, expressed in Hz, illuminates the surface of a solid, some electrons (i.e., photoelectrons) can be emitted if the incident photon energy, hν, is equal to or greater than the binding energy of the electron in the atom of the solid. Because the energy transfer occurs between photons and electrons, this behavior is called the ***photoelectric effect***. More precisely, Einstein demonstrated in the early 20th century that the ***maximum kinetic energy***, K_{max}, released by electromagnetic radiation to photoelectrons is given by the energy difference between the incident photon energy and electron binding energy in the atoms of a solid: $K_{max} = h\nu - h\nu_0$, where $B = h\nu_0$ is the ***binding energy*** of the electron inside the solid, which corresponds to the ***electron work function*** in the emitting material, i.e., $e\Phi$. For a given incident radiation energy, the ratio between the number of photoelectrons and the number of incident photons is called the ***photoelectric***

Table 9.9. Photocathode metals and alloys

Photocathode materials	Electron work function (W_S/eV)	Wavelength (λ/nm)	Photoelectric quantum yield (*Y*/nil)
Lithium	2.4	517	10^{-4}
Sodium	2.2	564	10^{-4}
Potassium	2.2	564	10^{-4}
Rubidium	2.1	591	10^{-4}
Cesium	1.9	653	10^{-4}
Calcium	2.9	428	10^{-4}
Strontium	2.7	459	10^{-4}
Barium	2.5	496	10^{-4}
Na_3Sb	3.1	400	0.02
K_3Sb	2.6	478	0.07
Rb_3Sb	2.2	564	0.10
Cs_3Sb	2.05	605	0.25
NaK_3Sb	2.0	620	0.30
$CsNaK_3Sb$	1.55	800	0.40

Note: The correspondence between the energy of the incident photon expressed in electron-volts and the wavelength expressed in nanometers of the associated electromagnetic radiation is given by the Duane and Hunt relation: $\lambda(/\text{nm}) = 1239.85207/E(/\text{eV})$.

quantum yield or ***efficiency***. Owing to the order of magnitude of binding electronic energies, the photoelectric effect occurs in metals for electromagnetic radiations having a frequency higher than that of near ultraviolet. Even if all solid materials exhibit a photoelectric effect under irradiation by an appropriate electromagnetic radiation (e.g., UV, X-rays, gamma-rays), the common metals exhibiting photoelectric effect for low-energy photons and currently used as photocathodes are the alkali and alkali-earth metals and some of their alloys deposited onto an antimony coating. For instance, rhenium metal, with an electronic work function of roughly 5.0 eV, requires at least a UV radiation with a wavelength of 248 nm for emitting photoelectrons, while cesium requires only irradiation by visible light with wavelengths of 652 nm or lower. Selected properties of some common photocathode materials are listed in Table 9.9. As a general rule, photocathode materials are extensively used in photocells and photomultiplier tubes.

NB: It is important to make the clear distinction between the photoelectric effect, which occurs during the extraction of electrons of an atom that are part of a crystal lattice in a solid by an incident electromagnetic radiation, and ***photoemission***, which consists of the extraction of electrons (i.e., ionization) of a free atom in a vapor by an incident electromagnetic radiation.

9.5 Secondary Emission

When a flux of electrons is incident upon a surface of a solid, secondary electrons are produced and emitted in a vacuum. These secondary electrons can be grouped into several types according to their origin: true secondary electrons with a kinetic energy of about 10 eV

Table 9.10. Secondary emission characteristics of selected materials

Material	Maximum incident energy (E_{max}/eV)	Maximum secondary emission coefficient (δ_{max})	Material	Maximum incident energy (E_{max}/eV)	Maximum secondary emission coefficient (δ_{max})
Ferrous Metals			**Halides**		
Iron	200	1.30	CsCl	n.a.	6.50
Cobalt	500	1.35	LiF	n.a.	5.60
Nickel	450	1.35	NaF	n.a.	5.70
Common Nonferrous			NaBr	n.a.	6.30
Copper	600	1.28	NaCl	600	6.80
Other metals			KCl	1500	8.00
Beryllium	200	0.50	**Oxides and Sulfides**		
Barium	300	0.85	BeO	400	8.00
Caesium	400	0.72	MgO	1600	15
Platinum-group metals (PGMs)			Al_2O_3	1300	3.00
Palladium	550	1.65	Cu_2O	440	1.20
Ruthenium	570	1.40	SiO_2	300	2.20
Iridium	700	1.50	ZnS	350	1.80
Platinum	720	1.60	MoS_2	n.a.	1.10
Reactive and refractory metals (groups IVB, VB, and VIB)					
Titanium	280	0.90	Niobium	350	1.20
Zirconium	350	1.10	Tantalum	600	1.25
Chromium	400	1.10	Molybdenum	350	1.20
Tungsten	650	1.35	Thorium	800	1.10

independent to that of the primary energy and primary electrons scattered both elastically (i.e., coherent scattering) and inelastically (i.e., incoherent scattering). The dimensionless ratio of secondary electrons to other primary electrons is called the ***secondary emission coefficient***, denoted δ. The secondary emission coefficient reaches a maximum value, δ_{max}, for a definite maximum energy of incident electrons, E_{max}, and afterwards decrease slowly for higher kinetic energies.

9.6 Electrolytes

Electrolytes are distinguished from pure electronic conductors by the fact that the passage of an electric current is only insured by displacement of charged species called ions and hence accompanied by a transfer of matter. Therefore, electrolytes are entirely ionic electrical conductors without exhibiting any electronic conductivity (i.e., no free electrons). They can be found in the solid state (e.g., fluorite, beta-aluminas, yttria-stabilized zirconia, and silver iodide), liquid state (e.g., aqueous solutions, organic solvents, molten salts and ionic liquids), and gaseous state (e.g., ionized gases and plasmas). The ions (i.e., anions or cations) ensure the proper ionic conductivity by moving under the electrical field imposed by the electrodes. Usually, electrolytes can be grouped into three main classes:

- **Pure electrolytes.** This class is entirely represented by molten or fused salts (e.g., molten cryolite, Na_3AlF_6) and usually requires high temperatures—largely above the melting or liquidus temperature of the salt—to provide sufficient ionic conductivity.
- **Ionic solutions.** This class is represented by electrolytic solutions and is also split into two subclasses according to ionic conductivity and dissociation constant.
  - **Strong electrolytes** (ionophores)**.** Potassium chloride (KCl) is the main example of the class of ionophores, that is, pure ionic compounds (solids, liquids, or gases) already made of anions and cations. The dissolution of these ionophores simply involves the dispersion of preexisting ions of the crystal lattice into an appropriate solvent followed by a reorganization of solvent molecules around ions (i.e., the solvation process). This phenomenon strongly depends on the relative electric permittivity ε_r (i.e., formerly the dielectric constant) of the solvent. Actually, in ionizing solvents—those, like water ($\varepsilon_r = 78.36$ at 298.15K), having a high electric permittivity—the coulombic interaction between ions is strongly decreased. Hence, ions maintain a certain independence in their displacement, and they are totally dissociated (i.e., ionized). By contrast, in inert solvents (e.g., benzene)—those exhibiting a low electric permittivity—ionic entities such as pairs or clusters form, losing their freedom. For instance, in a series of solvents of decreasing permittivity, ions form double, triple, and quadruple associations such as $LiBF_4$ in dimethoxyethane ($\varepsilon_r = 7.15$ at 298.15K).
  - **Weak electrolytes.** In this case the solute is only partially ionized (e.g., NH_4Cl in water). Salts obtained by the neutralization of a weak acid by a strong base (e.g., $CH_3COO^-Na^+$), a weak base by a strong acid (e.g., NH_4Cl), or a weak acid by a weak base (e.g., $CH_3COO^-NH_4^+$) are typical examples of weak electrolytes.
- **Solid electrolytes.** These correspond to solid materials in which the ionic mobility is insured by various intrinsic and extrinsic defects and are called ***solid ion conductors***. Common examples are ion-conducting solids with rock salt or halite-type solids with a B1 structure (e.g., α-AgI), oxygen-conducting solids with a fluorite-type C1 structure ($A^{II}O_2$), for instance CaF_2 and yttria-stabilized zirconia (YSZ, ZrO_2 with 8 mol.% Y_2O_3), a pyrochlore structure ($A_2B_2O_7$), perovskite-type oxides ($A^{II}B^{IV}O_3$), $La_2Mo_2O_9$, or solids with the spinel-type structure such as beta-aluminas ($NaAl_{11}O_{17}$) for which the ionic conduction is ensured by Na^+ mobility.

See Table 9.11.

9.7 Electrode Materials

9.7.1 Electrode Materials for Batteries and Fuel Cells

In power sources, i.e., primary and secondary batteries, and fuel cells, the electrode material of both cathode and anode must exhibit a high standard electrode potential expressed in volts (V). Actually, an anode material must be highly electropositive, i.e., reducing, while a cathode material must be highly electronegative, i.e., oxidizing. The second important physical quantity required to select the most appropriate electrode material is its electrochemical equivalence. The ***electrochemical equivalence***, denoted Eq, of an electrode material expresses the available electric charge stored per unit mass of material, and hence it is expressed in $C.kg^{-1}$ ($Ah.g^{-1}$) and calculated with the following equation:

$$Eq = n{\cdot}F/\nu{\cdot}M,$$

Table 9.11. Ionic conductivity of various electrolytes

Molten oxide		Ionic conductivity (κ/ S.m^{-1})	Molten-salt electrolyte		Ionic conductivity (κ/ S.m^{-1})	Aqueous electrolyte		Ionic conductivity (κ/ S.m^{-1})	Solid-state ionic conductor		Ionic conductivity (κ/ S.m^{-1})
Pure molten oxides[1]	FeO (1370°C)	12,200	Pure molten inorganic salts	LiF (1000°C)	920	Aqueous electrolytes	H_2O (distilled)	5.5×10^{-6}	Solid state ionic conductor	Yttria-stabilized zirconia (8–10 mol.% Y_2O_3)	0.2 (800°C) 0.3 (900°C) 1.0 (1000°C)
	TiO_2 (1850°C)	10,000		NaF (1000°C)	494		HCl (20 wt.%)	76		Ceria stabilized zirconia	0.6 (1200°C)
	MgO (2800°C)	3500		KF (980°C)	392		H_2SO_4 (30 wt.%)	74		Fluorite (CaF_2)	
	CaO (2580°C)	4000		LiCl (801°C)	659		KOH (30 wt.%)	54		Silver iodide (AgI)	10 (150°C)
				NaCl (1000°C)	416		NaOH (15 wt.%)	35		Beta-aluminas ($NaAl_{11}O_{17}$)	3–5
	Al_2O_3 (2050°C)	1500		KCl (1200°C)	265		KCl (21 wt.%)	28		Titania-rich chloride slag (1600°C)	30
				CaF_2 (1500°C)	410		NaCl (26 wt.%)	22			
	SiO_2 (1710°C)	0.1		$CaCl_2$ (1000°C)	266		$CaCl_2$ (25 wt.%)	18		Semigraphite	1.125×10^5
				$MgCl_2$ (1000°C)	158						

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[1] Pure molten oxide above materials' melting temperature. Note that low conductivity is typical of network-forming oxides such as silica and alumina, while iron oxide and titania exhibit the highest conductance.

Table 9.12. Electrochemical equivalents of common anode and cathode materials used in primary and secondary cells (293.15 K and 101.325 kPa)

Electrode material		Half-reaction electrochemical reaction	E^0_{298} (V/SHE)	M_r[2] ($^{12}C = 12$)	Density[3,4,5] ($kg.m^{-3}$)	Eq ($Ahkg^{-1}$)	Eq ($Ahdm^{-3}$)
Anode materials (negative)	Al	Al^0 —> $Al^{3+} + 3e^-$	−1.676	26.981538	2699	2980	8043
	Ca	Ca^0 —> $Ca^{2+} + 2e^-$	−2.840	40.078	1550	1337	2073
	Cd	Cd^0 —> $Cd^{2+} + 2e^-$	−0.403	112.411	8650	477	4125
	Fe	Fe^0 —> $Fe^{2+} + 2e^-$	−0.440	55.845	7874	960	7558
	$H_2(g)$	$H_2(g)$ —> $2H^+ + 2e^-$	0.000	2.01594	0.084	26,590	2234
	Li	Li^0 —> $Li^+ + e^-$	−3.040	6.941	534	3861	2062
	Mg	Mg^0 —> $Mg^{2+} + 2e^-$	−2.356	24.3050	1738	2205	3833
	Na	Na^0 —> $Na^+ + e^-$	−2.713	22.989770	971	1166	1132
	Pb	Pb^0 —> $Pb^{2+} + 2e^-$	−0.126	207.2	11,350	259	2936
	Zn	Zn^0 —> $Zn^{2+} + 2e^-$	−0.760	65.409	7133	820	5846
Cathode materials (positive)	Ag_2O	$Ag^+ + e^-$ —> Ag^0	+0.7991	231.7358	7200	231	1665
	AgO	$AgO + 2H^+ + e^-$ —> $Ag^0 + H_2O$	+1.772	123.8676	7500	433	3246
	$Cl_2(g)$	$Cl_2 + 2e^-$ —> $2Cl^-$	+1.360	70.906	2948	756	2229
	HgO	$HgO + 2H^+ + 2e^-$ —> $Hg^0 + H_2O$	+0.926	216.5894	11,140	248	2757
	$I_2(s)$	$I_2(s) + 2e^-$ —> $2I^-$	+0.5356	253.80894	4933	212	1045
	MnO_2	$MnO_2 + 4H^+ + e^-$ –> $Mn^{3+} + 2H_2O$	+0.950	86.936849	5080	308	1566
	NiOOH	$2NiOOH + 2H^+ + 2e^-$ –> $2Ni(OH)_2$	+0.490	91.70017	7400	292	2160
	$O_2(g)$	$O_2 + 4H^+ + 4e^-$ —> $2H_2O$	+1.229	31.9988	1330	3350	4456
	PbO_2	$PbO_2 + 4H^+ + 2e^-$ –> $Pb^{2+} + H_2O$	+1.460	239.1988	9640	224	2160
	$SO_2(l)$	$2SO_2 + 2e^-$ —> $S_2O_4^{2-}$	n.a.	64.0638	1370	419	n.a.
	$SOCl_2(l)$	$2SOCl_2 + 4e^-$ —> $S + SO_2 + 4Cl^-$	n.a.	118.9704	1631	901	1470
	V_2O_5	$VO_2^+ + 2H^+ + e^-$ —> $VO^{2+} + H_2O$	1.000	181.880	3350	147	494

where n is the number of electrons required to oxidize or reduce the electrode material, F the Faraday constant 96,485.309 $C.mol^{-1}$, ν the dimensionless stoichiometric coefficient of the electrochemical reduction or oxidation, and M the atomic or molecular mass of the electrode material in $kg.mol^{-1}$ ($g.mol^{-1}$). Sometimes the electrochemical equivalence per unit volume is used, and it is expressed as the electric charge stored per unit volume of material ($Ah.m^{-3}$); in this particular case, it can be calculated multiplying the specific electrochemical equivalence by the density of the electrode material.

In addition, in primary and rechargeable batteries, apart from the two previous scientific parameters, several technological requirements must be considered when selecting the most appropriate electrode. These requirements are high electrical conductivity, chemical inertness,

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[2] Standard relative atomic masses from: Loss, R.D. (2003) *Atomic Weights of the Elements 2001. Pure Appl. Chem.*, **75**(8), 1107–1111.

[3] Densities of pure elements from: Cardarelli, F. (2001) *Materials Handbook. A Concise Desktop Reference.* Springer, Berlin Heidelberg New York.

[4] Densities of inorganic compounds from: Lide, D.R. (ed.) (1997–1998) *CRC Handbook of Chemistry and Physics,* 78th ed. CRC Press, Boca Raton, FL, pp. 4–35 to 4–9.

[5] Densities for ideal gases calculated with equation $\rho = PM/RT$ at 293.15 K and 101.325 kP.

ease of fabrication, involvement of nonstrategic materials, low cost, and finally commercial availability. As a general rule, metals and alloys represent the major anode materials in batteries, except for the particular case of hydrogen in fuel cells, while metallic oxides, hydroxides, chlorides, and sulfides represent the major anodic materials, except oxygen, in fuel cells.

9.7.2 Intercalation Compounds

Insertion, also called intercalation, is a topotactic reaction that consists of the insertion of a species, atom, or molecule inside the interstitial crystal lattice of a solid host material, with or without charge transfer. Historically, the first intercalation compounds were the graphites (1841) for which the intercalation of cations of alkali metals occurred between the graphene lamellar planes and the hydrogen/palladium system (1866). Later, in 1959, the phenomenon was recorded in lamellar dichalcogenides and since the 1970s hundreds of new compounds have been reported, several of them now being used in rechargeable batteries such as Ni-MH or lithium batteries.

In the particular case of lithiation or delithiation of cathode materials used in lithium secondary batteries, the calculation of the electrochemical equivalent involves an additional parameter related to the reaction of intercalation of lithium cations into the crystal lattice of the host cathode materials. Consider the theoretical reversible reaction of intercalation of lithium into a crystal lattice of a solid host material (e.g., oxide, sulfide):

$$x\mathrm{Li}^{+} + y\mathrm{M} + xe^{-} <\!\!—\!\!> \mathrm{Li}_{x}\mathrm{M}_{y}$$

with	Li^{+}	lithium cations,
	M	solid host cathode material,
	x,y	dimensionless stoichiometric coefficients,
	x	dimensionless number of electrons exchanged.

Hence during the lithiation reaction (i.e., charge), x moles of lithium cations are reduced and intercalated into y moles of the solid host material, and a quantity of electricity, xF, must be supplied to the cell. Conversely, during delithiation (i.e., discharge), x moles of lithium cations are produced and a quantity of electricity, xF, is supplied to the external circuit of the cell. Therefore, the quantity of electricity, Q, expressed in coulombs (Ah), delivered following the deintercalation of lithium from a mass, m_{M}, of the solid host material or a mass, m_{LixMy}, of the final intercalated compound is given by the two following relations:

$$Q = m_{\mathrm{M}} \,.\, (xF/yM_{\mathrm{M}}) = m_{\mathrm{LixMy}} \,.\, (xF/M_{\mathrm{LixMy}}),$$

with	m_{M}	mass of the solid host material, in kg,
	m_{LixMy}	mass of the intercalated compound, in kg,
	x, y	dimensionless stoichiometric coefficients,
	M_{M}	molar mass of the solid host materials, in $\mathrm{kg.mol}^{-1}$,
	M_{LixMy}	molar mass of the intercalated compounds, in $\mathrm{kg.mol}^{-1}$,
	x	dimensionless number of electrons exchanged,
	F	Faraday constant $F = 96{,}485.309\ \mathrm{C.mol}^{-1}$.

From the above equation it is possible to define two types of electrochemical equivalents. The first electrochemical equivalent, denoted $E_{\mathrm{q}}(\mathrm{M})$, is the quantity of electricity consumed per unit mass of the solid host material, M, during the lithiation reaction (i.e., charging) and is defined by the following equation:

$$E_{\mathrm{q}}(\mathrm{M}) = xF/yM_{\mathrm{M}}.$$

Table 9.13. Electrochemical equivalents of solid host materials and intercalated compounds for rechargeable lithium batteries

Host cathode material	Insertion reaction (lithiation/delithiation)	E^0_{298} (V/Li^+)	M_r[6] (Li_xM_y) (M)	Density[7] ($kg.m^{-3}$) (M)	E_q (Li_xM_y) ($Ahkg^{-1}$)	E_q(M) ($Ahkg^{-1}$)	E_m ($Wh.kg^{-3}$)
C	$Li^+ + 6C + e^- <—> LiC_6$		79.0070 12.011	2200	339	372	
FeS_2	$Li^+ + FeS_2 + e^- <—> LiFeS_2$		126.9180 119.9770	5020	211	223	
$FePO_4$	$Li^+ + FePO_4 + e^- <—> LiFePO_4$		157.7574 150.8164		167	178	
$Li_{1.2}V_3O_8$	$2.8Li^+ + Li_{1.2}V_3O_8 + 2.8e^-$ $<—> Li_4V_3O_8$		308.5837 289.1489		243	260	
$Li_{0.5}CoO_2$	$0.5Li^+ + Li_{0.5}CoO_2 + 0.5e^-$ $<—> LiCoO_2$	3.7	97.8730 94.4025		137	142	
$Li_{0.5}NiO_2$	$0.5Li^+ + Li_{0.5}NiO_2 + 0.5e^-$ $<—> LiNiO_2$	3.5	97.6332 94.1627		137	142	
$Li_4Ti_5O_{12}$	$3Li^+ + Li_4Ti_5O_{12} + 3e^-$ $<—> Li_7Ti_5O_{12}$	1.5	484.9148 464.0918		167	173	
MnO_2	$0.7Li^+ + MnO_2 + 0.7e^-$ $<—> Li_{0.7}MnO_2$	3.0	91.7956 86.9369	5080	204	216	
MoS_2	$0.8Li^+ + MoS_2 + 0.8e^-$ $<—> Li_{0.8}MoS_2$	1.7	165.6248 160.0720	5060	130	134	
TiS_2	$Li^+ + TiS_2 + e^- <—> LiTiS_2$	2.1	118.940 112.999	3370	225	237	
V_2O_5	$1.2Li^+ + V_2O_5 + 1.2e^-$ $<—> Li_{1.2}V_2O_5$	2.8	190.2092 181.8800	3350	170	177	
VO_x	$2.5Li^+ + VO_x + 2.5e^- <—> Li_{2.5}VO_x$	2.3					
WO_2	$Li^+ + WO_2 + e^- <—> LiWO_2$		222.7798 215.8388	10,800	120	124	

The second electrochemical equivalent, denoted $E_q(Li_xM_y)$, is the quantity of electricity released per unit mass of the intercalated compound, Li_xM_y, during the delithiation reaction (i.e., discharging) and is defined by the following equation:

$$E_q(Li_xM_y) = xF/M_{LixMy}.$$

The two electrochemical equivalents of some selected solid host cathode materials and corresponding intercalated compounds used in rechargeable lithium batteries are presented in Table 9.13.

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[6] Standard relative atomic masses from: Loss, R.D. *(2003) Atomic Weights of the Elements* 2001. *Pure Appl. Chem.*, 75(8), 1107–1111.

[7] Densities taken from: Lide, D.R. (ed.) (1998–1999) *CRC Handbook of Chemistry and Physics,* 78th ed. CRC Press, Boca Raton, FL, pp. 4–35 to 4–9.

9.7.3 Electrode Materials for Electrolytic Cells

Today, in modern the chemical process industry, electrochemistry occupies an important place. Electrochemical processes are actually widely used in the inorganic syntheses.[8] Actually, it is the only method for preparing and recovering several pure elements (e.g., aluminum, magnesium, alkali and alkali-earth metals, chlorine, and fluorine).[9] Furthermore, it occupies an important place in hydrometallurgy for electrowinning and electrorefining metals of groups IB (e.g., Cu, Ag, Au), IIB (e.g., Zn, Cd), and IVA (e.g., Sn, Pb).[10,11] In addition, its development also concerns organic synthesis, where some processes reach industrial scale (e.g., Monsanto, Nalco, and Philips processes).[12] Apart from electrochemical processes for preparing inorganic and organic compounds, other electrolytic processes are also used in various fields: in extractive hydrometallurgy (e.g., the electrolytic recovery of zinc[13]), in zinc electroplating (e.g., high-speed electrogalvanizing of steel plates[14]), in electrodialysis (e.g., the salt-splitting regeneration of sulfuric acid and sodium hydroxide from sodium sulfate waste brines,[15,16] the regeneration of the leaching solutions of uranium ores, the electrolytic regeneration of spent pickling solutions[17]), and finally in processes for a cleaner environment, where electrochemistry is used to achieve the electrooxidation of organic pollutants (i.e., electrolytic mineralization or electroincineration), and in the removal of hazardous metal cations from liquid wastes effluents.[18]

Electrochemical processes are performed in an electrolytic cell[19] (i.e., ***electrolyser***). The electrolyzer is a reactor vessel, filled with an electrolytic bath or ***electrolyte***, in which the electrodes are immersed and electrically connected via busbars to a power supply. When the electrolyzer is split into two compartments by a ***separator*** (e.g., diaphragm, membrane), the electrolyte has two different compositions (i.e., ***anolyte*** and ***catholyte***). The electrodes are the main parts of an electrolyzer and consist of the ***anode*** (i.e., positive, +) where the oxidation reaction occurs, while at the ***cathode*** (i.e., negative, –) a reduction takes place. Among the several issues encountered by engineers for designing an industrial electrochemical reactor, one of them consists in reducing the specific electric energy consumption (i.e., electric energy per unit mass of product). The specific energy consumption can be minimized in two ways: increasing the current efficiency and lowering the operating cell voltage. Other issues for designing electrochemical cells are discussed in more detail elsewhere in the literature.[20,21,22]

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[13] Karavasteva, M.; Karaivanov, St. (1993) Electrowinning of zinc at high current density in the presence of some surfactants. *J. Appl. Electrochem.*, **23**(7), 763–765.

[14] Hardee, K.L.; Mitchell, L.K.; Rudd, E.D. (1989) *Plat. Surf. Finish.*, **76**(4), 68.

[15] Thompson, J.; Genders, D. (1992) Process for producing sodium hydroxide and ammonium sulfate from sodium sulfate. US Patent 5,098,532; March 24, 1992.

[16] Pletcher, D.; Genders, J.D.; Weinberg, N.L.; Spiegel, E.F. (1993) Electrochemical methods for production of alkali metal hydroxides without the co-production of chlorine. US Patent 5,246,551; September 21, 1993.

[17] Schneider, L. (1995) Process and apparatus for regenerating an aqueous solution containing metal ions and sulfuric acid. US Patent 5,478,448; December 26, 1995.

[18] Genders, D.; Weinberg, N.L. (eds.) (1992) *Electrochemistry for a Cleaner Environment.* Electrosynthesis Co., Lancaster, NY.

[19] Wendt, S.; Kreysa, G. (1999) *Electrochemical Engineering.* Springer, Berlin Heidelberg New York.

[20] Pickett, D.J. (1979) *Electrochemical Reactor Design.* Elsevier, Amsterdam.

[21] Rousar, I.; Micka, K.; Kimla, A. (1985) *Electrochemical Engineering,* Vols. 1 and 2. Elsevier, Amsterdam.

The overall cell voltage at a given current density, U_{cell}, can be classically described as the following algebraic sum:

$$\Delta U_{cell} = \Sigma_k(E_{a,th} - E_{c,th}) + \Sigma_k(\eta_{a,k} - \eta_{c,k}) + i\Sigma_k R_k + \Delta U_t = \Delta U_{th} + \Delta\eta + iR_{tot} + \Delta U_t,$$

where the first term corresponds to the Nernstian theoretical or thermodynamic cell voltage and consists of the algebraic difference between the thermodynamic potentials of the anode and cathode respectively (i.e., Nernst electrode potentials), the second term is the summation of all the ***electrode overpotentials*** (e.g., activation, concentration, passivation, etc.), the third term is the summation of all the ***ohmic drops*** (e.g., electrolytes, both anolyte and catholyte, separators, connectors, and busbars), and finally cell potential drift is due to the aging of electrodes (e.g., corrosion, deactivation, and passivation) and/or separator materials (e.g., fooling, degradation, and swelling).

Hence, the operating cell voltage could be reduced In several ways.[23] First, an appropriate counter electrode reaction minimizes the reversible cell voltage. Second, a narrow interelectrode gap and electrode-membrane gap in association with a highly conductive electrolyte and separator and highly conductive metals for busbars, feeders, and connectors diminish the overall ohmic drop. Third, turbulent promoters should be used to enhance convection and hence the mass transfer coefficient in order to reduce the concentration overpotential. Finally, the activation overpotential could be reduced by using an efficient and appropriate electrocatalyst. The selection of a catalyst is an important problem to solve, particularly in the case of oxygen or chlorine anodes. For theoretical aspects of electrocatalysis, they are reviewed extensively in more detail by Trasatti.[24] Indeed, because of the complex behavior of electrodes, the selection of an electrocatalyst for a given process cannot be made simply on the basis of electrochemical kinetic considerations (i.e., exchange current density, Tafel slopes). An experimental approach is compulsory. Actually, the prediction of an electrode's service life requires real standardized tests (i.e., accelerated service-life tests). For the practicing engineer, several scientific and technical criteria must be considered when selecting an appropriate electrode material. Therefore, electrode materials must exhibit the following requirements:

(i) high exchange current density (j_o) and a good electron transfer coefficient (α or β) for the selected electrochemical reaction to decrease activation overpotential;
(ii) good electronic conductivity to decrease the ohmic drop and the Joule's heating;
(iii) good corrosion resistance to both chemical and electrochemical reactions, combined with no passivating and blistering behavior, leading to abnormal electrode degradation and consumption;
(iv) a good set of mechanical properties suited for industrial use (i.e., low density, high tensile strength, stiffness);
(v) ease of fabrication (i.e., machining, joining, and cleaning) allowing one to obtain clean and intricate shapes;
(vi) low cost combined with commercial availability and a wide variety of products (e.g., rod, sheet, expanded metal);
(vii) nonhazardous, nontoxic, and environmentally friendly material.

It is important to note that the combination of criteria (3) and (4) is essential for the dimensional stability of an electrode and its service life.

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[23] Couper, A.M.; Pletcher, D.; Walsh, F.C. (1990) Electrode materials for electrosynthesis. *Chem. Rev.*, **90**(5), 837–865.

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9.7.3.1 Industrial Cathode Materials

Generally speaking, the selection of a cathode material is easier for the electrochemist or the electrochemical engineer than selecting an anode material. Actually, given that the most important factor in selecting a cathode material is the overpotential for the evolution of hydrogen, there exists a wide range of electronically conductive materials with the desired overpotential for both acid and alkaline electrolytes. For instance, some metals exhibit a high overpotential (e.g., Cd, Pb, Hg), while other materials are characterized by a low overpotential (e.g, Pt, Cu, Ag, platinized C, and Ni). The second most important factor is the stability of the cathode material toward nascent hydrogen gas evolved during the cathodic polarization of the material. Several refractory metals used as cathodes (e.g., Ti, Nb, Ta, Fe, and steels) are prone to hydrogen pickup and hence are extremely sensitive to hydrogen embrittlement, which leads to the blistering or even spalling of the metal affecting its dimensional stability. Therefore, these metals are not suited for the type of manufacturing cathodes that must be used in aqueous electrolytes.

9.7.3.1.1 Low-Carbon Steel Cathodes

Low-carbon steel exhibits a low hydrogen overpotential and a low cost and can be obtained in a wide variety of mill products. In addition, with its ease of fabrication, joining, and cleaning, it is the standard cathode material in the chlor-alkali industry in either the membrane or diaphragm processes. If cathodically polarized during shutdowns and carefully handled, it offers an unlimited service life. When the hydrogen overpotential must be decreased, Ni- and Co-based coatings can be applied onto it by electrochemical or thermal decomposition techniques. Sometimes a Ni-Zn or Ni-Al coating is deposited and the Zn or Al is later removed by an alkaline hot leach with 50 wt.% NaOH, leaving a Raney nickel catalyst, greatly enhancing the active surface area. Recently, noble-metal coatings, combined with the introduction of a catalyst into the electrolyte, have also been reported in the literature.

9.7.3.1.2 Aluminum Cathodes

Aluminum metal and, to a lesser extent, aluminum alloys are suitable materials for manufacturing industrial cathodes. Actually, pure aluminum metal exhibits a low density (2690 $kg.m^{-3}$) and high thermal conductivity (237 $Wm^{-1}K^{-1}$), is a good electrical conductor (2.6548 μΩ.cm), does not form hydride with nascent hydrogen, and passivates when polarized anodically. All these characteristics, along with a reasonable average cost of 2.734 US$/kg (for 99.7 wt.% Al), are major assets for its wide utilization especially in zinc electrowinning.

Industrial applications. In zinc electrowinning, zinc is directly plated onto aluminum cathodes while oxygen is evolved at the Pb-Ag anode. Once the zinc electrodeposit reaches a desired thickness, the aluminum cathodes are removed from the cells, followed by either manually or automatically stripping the zinc deposit. On the other hand, molten aluminum is used as liquid cathode during the electrowinning of aluminum in the Hall–Heroult process.

Failure modes. In zinc electrowinning, when the cathodes are lifted from the electrolyte, removed from the cells, and stripped, some corrosive sulfate electrolyte remains on the surface of the cathodes despite the water rinsing treatment. As a result, the cathodes, especially in the area close to the edges of the cathode, is corroded to a varying degree, depending on the amount and concentration of the acid in contact with the cathode. Evaporation of the electrolyte is also observed at the surface of the cathode, resulting in precipitation of insoluble zinc-sulfate salts and other impurities, causing an increase in the corrosion rate of the aluminum cathode. The overall effect of this corrosion attack can be seen on the smoothness of the aluminum cathode, i.e., patches of rough areas appear at times on the surface of the aluminum. Because of the unevenness in the surface of the cathode and of the presence of impurities, the zinc deposition process is affected resulting in the formation of rough zinc deposits. Usually, these areas are seen as "puffed" sections of the deposits that, because of their closer proximity to the anode, tend to affect the current distribution in the electrolysis cell. As the zinc electrowinning process is sensitive to variations in current density, the uneven current distribution observed with puffed zinc deposits causes a decrease in the current efficiency of zinc deposition. Under these conditions, higher corrosion rates of the Pb-Ag anode are observed that result in an increase in the Pb content of the zinc deposits. Another effect of the impurities on the surface of the aluminum cathode is the formation of pinholes on the zinc deposit. This also results in lower current efficiency of zinc deposition. A known method of preventing the occurrence of puffed zinc deposits consists of mechanically or manually buffing the aluminum cathodes using metal or plastic brushes. Mechanical buffing is carried out using automated machines that apply a scrubbing action at the surface of the cathode. As a result the surface of the cathode is maintained free of deposited impurities. However, due to the presence of edge strips located at the sides and bottom of the aluminum cathode to prevent electrodeposition of zinc on the sides of the cathode and facilitate the stripping of the deposits, the mechanical buffing machines are not efficient in treating the entire surface of the cathode. Furthermore, mechanical or manual buffing of the affected cathodes does not completely remove the deposited impurities, and insoluble zinc-sulfate salts from the surface of the electrode as the treated areas become affected after about three weeks, necessitating rebuffing of the electrode. To facilitate removal of impurities and insoluble zinc-sulfate salts from an aluminum cathode used in zinc electrowinning, a chemical treatment has been developed consisting of a mild HCl cleaning and water rinsing.

9.7.3.1.3 Titanium Cathodes

Titanium metal is a light metal with near half the density of copper (4540 kg.m^{-3}), exhibits an excellent strength-to-density ratio allowing one to use thinner and lightweight anode plates without sacrificing the mechanical stiffness of the cathode, and has an excellent corrosion resistance to various corrosive environments. The only drawbacks of titanium are its high electrical resistivity (42 μΩ.cm) and the high cost of the mill products (e.g., sheet, plate, rods), which can reach 46 US$/kg in some cases.

Titanium grades. The common titanium grades used in electroplating as cathodes are the chemically pure titanium such as ASTM grades 1 or 2, while for more demanding applications, especially when corrosion resistance to reducing acid is a requirement, titanium when alloyed with palladium (Ti-0.15Pd), like ASTM grades 7 and 11, or recently with ruthenium (Ti-0.10Ru) like ASTM grades 26 and 27, is recommended despite being more expensive than C.P. titanium.

Industrial applications. Electrorefining of copper is based on the unsupported process using permanent titanium cathode plates and an associated stripping machine. Electrolytic iron is also electrodeposited from ferrous-chloride or ferrous-sulfate baths onto titanium cathodes owing to the great ease of removal of the iron plate by mechanical stripping. Usually titanium must be etched with hot 20 wt.% HCl or a cold mixture of a fluoronitric mixture (HF-HNO_3) prior to performing the cathodic electrodeposition in order to remove the passivating rutile layer.

Failure modes. C.P. titanium metal and its alloys are susceptible to hydrogen pickup[25] and hence extremely sensitive to embrittlement by nascent hydrogen gas[26]; moreover in corrosive electrolytes the cathode must be polarized cathodically during shutdowns.

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[25] La Conti, A.B.; Fragala, A.R.; Boyack, J.R. (1977) *ECS Meeting*, Philadelphia, May 1977.

[26] Bishop, C.R.; Stern, M. (1961) Hydrogen embrittlement of tantalum in aqueous media. *Corrosion,* **17**, 379t–385t.

9.7.3.1.4 Zirconium Cathodes

Zirconium metal (6510 $kg.m^{-3}$) is denser but exhibits a better corrosion resistance and is less prone to hydrogen embrittlement than titanium metal. Moreover, zirconium is highly corrosion resistant in strong alkaline solutions and has a good inertness toward organic and inorganic acids. **Zirconium grades:** The most common zirconium grade used in electroplating is Zircadyne® 702.

9.7.3.1.5 Nickel Cathodes

Nickel, due to its immune behavior, is a strongly alkaline and especially concentrated solution of NaOH and KOH and, because it does not form hydride with hydrogen, is used extensively as a cathode in alkaline electrolytes.

9.7.3.1.6 Mercury Cathode

Mercury is the only liquid metal cathode used industrially in aqueous solutions due to its high overpotential for the evolution of hydrogen, which even allows it to electrodeposit alkali and alkali-earth metals from aqueous electrolytes, forming amalgams. For that reason, it was used extensively in the chlor-alkali industry despite being progressively phased out for both obvious health, safety, and environmental reasons. Moreover, with an average price of 580 US$ per UK flask (i.e., 76 lb.) in 2006, which corresponds to 16.8 US$/kg, it is an expensive material to use in large quantities such as those required in chlor-alkali plants.

See Tables 9.14–9.16, pages 566–568.

9.7.3.2 Industrial Anode Materials

Although the selection of the right material for an anode follows the same pattern as for cathode materials, this step still represents a critical issue in the final design of an industrial electrolyzer due to the particular operating conditions that anodes must withstand. Actually, historically, the failure of the anode has often led to the abandonment of some industrial processes. For instance, in aqueous solutions, a major problem arises because the anode is the electrode where the electrochemical oxidation occurs; hence the anode material must withstand harsh conditions due to both the elevated positive potential and the high acidity of the electrolyte. Moreover, traces of impurities in the electrolyte might be an additional source of corrosion and deactivation in some cases. Therefore, the material selection process must always be based on: strong knowledge of previous methods and clear understanding of the properties of the materials involved, experimental results acquired from accelerated service-life tests performed in the laboratory, and finally field tests conducted over long periods of time. The following paragraphs present the most common anode materials available industrially with a brief historical background, key properties, their techniques of preparation, their failure modes, and major industrial applications.

Table 9.14. Cathode materials for hydrogen (H_2) evolution in acidic media

Overvoltage range	Cathode material	Electrolyte composition	Molarity (C/mol.dm^{-3})	Temperature (T/°C)	Cathodic Tafel slope (b_c/mV.log$_{10}j_0^{-1}$)	Exchange current density decimal logarithm (log$_{10}$ j_0/A.cm^{-2})	Absolute value of Overvoltage at 200 A.m^{-2} (η/mV)
Extralow hydrogen overvoltage	Iridium (Ir)	H_2SO_4	0.5	25	30	–.2.699	30
	Palladium (Pd)	HCl	1	25	30	–2.500	24
		H_2SO_4	1	25	29	–3.200	44
	Platinum (Pt)	HCl	1	25	29	–3.161	43
		H_2SO_4	2	25	25	–3.200	38
	Rhodium (Rh)	H_2SO_4	4	25	28	–3.200	42
	Ruthenium	HCl	1	25	30	–4.200	75
Low hydrogen overvoltage	Molybdenum (Mo)	HCl	0.1	25	104	–6.400	343
	Tungsten (W)	HCl	5.0	25	110	–5.000	363
	Nickel (Ni)	HCl	1.0	25	109	–5.222	384
		H_2SO_4	1.0	25	124	–5.200	434
	Silver (Ag)	HCl	5.0	25	120	–5.301	432
		H_2SO_4	1.0	25	120	–5.400	444
	Iron (Fe)	HCl	0.5	25	133	–5.180	425
		H_2SO_4	0.5	25	118	–5.650	466
	Gold (Au)	HCl	0.1	25	123	–5.500	468
		H_2SO_4	1.0	25	116	–5.400	430
			4.0	25	130	–6.500	624
	Copper (Cu)	HCl	0.1	25	120	–6.823	615
		H_2SO_4	0.5	25	120	–7.700	720
High hydrogen overvoltage	Niobium (Nb)	HCl	1	25	110	–9.000	803
		H_2SO_4	2	25	120	–8.400	804
	Titanium (Ti)	HCl	1	25	130	–7.500	754
		H_2SO_4	0.5	25	135	–8.200	877
			1	25	119	–8.150	767
	Tin (Sn)	H_2SO_4	4	25	120	–9.00	877
	Zinc (Zn)	HCl	1	25	120	–10.800	1092
		H_2SO_4	2	25	120	–10.800	1092
	Cadmium (Cd)	H_2SO_4	0.25	25	135	–10.769	1225
	Lead (Pb)	HCl	1	25	117	–12.900	1311
		H_2SO_4	0.5	25	120	–12.700	1320
	Mercury (Hg)	HCl	1	25	118	–12.500	1475
		H_2SO_4	2	25	119	–12.107	1239

$\eta_c = (E_{c,j} - E_{th}) = b_c(\log_{10}j_{eq} - \log_{10}j) = (\ln 10RT/\beta nF)\log_{10}j_{eq} - (\ln 10RT/\beta nF)\log_{10}j$

Table 9.15. Anode materials for oxygen (O_2) evolution in acidic media

Over-voltage range	Anode material	Electrolyte composition	Molarity (C/mol.dm^{-3})	Temperature (T/°C)	Anodic Tafel slope (b_a/mV.$\log_{10} j_0^{-1}$)	Exchange current density decimal logarithm ($\log_{10} j_0$/A.cm^{-2})	Overvoltage at 200 A.m^{-2} (mV)
Low oxygen overvoltage	Ta/Ta_2O_5-IrO_2	H_2SO_4 30%wt.	3.73	80	52 133	−3.630 −10.21	101
	Ti-Pd (Gr.7)/ Ta_2O_5-IrO_2	H_2SO_4 30%wt.	3.73	80	54 164	−4.53 −8.21	153
	Ti/TiO_2-IrO_2	H_2SO_4 30%wt.	3.73	80	60	−4.886	191
	Ti (Gr.2)/ Ta_2O_5-IrO_2	H_2SO_4 30%wt.	3.73	80	51 158	−5.82 −7.69	210
Medium oxygen overvoltage	Ti/TiO_2-RuO_2 (DSA®-Cl_2)	H_2SO_4	1	80	66	−7.900	409
		CF_3SO_3H	1	80	65	−8.000	410
	Ruthenium-iridium	H_2SO_4	1	80	74	−7.020	400
		CF_3SO_3H	1	80	86	−6.630	419
	Iridium (Ir)	H_2SO_4	1	80	85	−6.800	433
		CF_3SO_3H	1	80	84	−6.800	428
High oxygen overvoltage	alpha-PbO_2	H_2SO_4	4	30	45	−15.700	630
	Platinum-ruthenium	H_2SO_4	1	80	120	−7.700	710
		CF_3SO_3H	1	80	120	−7.500	670
	Platinum-rhodium	H_2SO_4	1	25	115	−7.600	679
	Rhodium (Rh)	$HClO_4$	1	25	125	−7.520	727
	Platinum (Pt)	H_2SO_4	1	80	90	−10.900	828
		CF_3SO_3H	1	80	94	−9.800	762
		$HClO_4$	1	25	110	−9.000	803
	Pt/MnO_2	H_2SO_4	0.5	25	110	n.a.	n.a.
	beta-PbO_2	H_2SO_4	4	30	120	−9.200	900
	PbO_2	H_2SO_4	4	30	120	−10.000	996
	Ti_4O_7 (Ebonex®, bare)	H_2SO_4	1	25	n.a.	n.a.	1800

$\eta_a = (E_{a,j} - E_{th}) = b_a(\log_{10} j - \log_{10} j_{eq}) = (\ln 10 RT/\alpha nF)\log_{10} j - (\ln 10 RT/\alpha nF)\log_{10} j_{eq}$

Table 9.16. Anode materials for chlorine (Cl_2) evolution

Over-voltage range	Anode material (wt.%)	Electrolyte composition	Molarity (C/mol.dm^{-3})	Tempera-ture (T/°C)	Anodic Tafel slope (b_a/mV.$\log_{10} j_0^{-1}$)	Exchange current density decadic logarithm ($\log_{10} j_0$/A.cm^{-2})	Anodic overvoltage at 5 kA.m^{-2} (/V)
Low chlorine overpotential	Pt30-Ir70	NaCl	Satd.	65			0.000
	Ti/TiO_2-RuO_2-SnO_2 (61-31-8)	NaCl	Satd.	65			+0.020 to +0.060
	Ti/TiO_2-RuO_2 (83-17)	NaCl	Satd.	65			+0.025 to +0.076
	Ti/TiO_2-RuO_2 (65-35)	HCl	1	25	30	−1.409	+0.043
		NaCl	5	20	108	−1.409	+0.152
	Ti/Ta_2O_5-RuO_2-IrO_2 (89-6-5)	NaCl	Satd	65			+0.090
	Ti/MnO_2	NaCl	6	25	20–110	−4.000 to −2.273	+0.080 to +0.250
		HCl	1	20	37	−2.8861	+0.107
	Ti/Ta_2O_5-RuO_2-IrO_2 (79-11-10)	NaCl	Satd	65			+0.140
High chlorine overpotential	Graphite	HCl	18	80	70	−4.286	+0.440
	Ti/MnO_2-SnO_2 (56-44)	NaCl	Satd.	65	n.a.	n.a.	+0.620
	Fe_3O_4	NaCl	5.3	25	73	−7.796	+0.569
		NaCl	2	25	90	−7.796	+0.702
	PbO_2	NaCl	6	25	150–200	−4.174 to −4.097	+0.626 to +0.819
	Platinum (Pt)	NaCl	2	85	250	−4.200	+1.050
		NaCl	2	25	290	−3.700	+1.073
		NaCl	5	25	305	−3.700	+1.129

$\eta_a = (E_{a,j} - E_{th}) = b_a(\log_{10} j - \log_{10} j_{eq}) = (\ln 10 RT/\alpha nF)\log_{10} j - (\ln 10 RT/\alpha nF)\log_{10} j_{eq}$

9.7.3.2.1 Precious- and Noble-Metal Anodes

Electrochemists early on observed that noble and precious metals were stiff materials, with good tensile properties and machinability, high electronic conductivity, and exceptional chemical and electrochemical inertness in most corrosive media,[27] all combined with intrinsic electrocatalytic properties.[28] Consequently, the first industrial anodes used in electrochemical processes requiring an excellent dimensional stability were made of the noble and precious metals (e.g., Au and Ag), the six platinum-group metals (PGMs) (e.g., Ru, Rh, Pd, Os, Ir, and Pt), or their alloys (e.g., ^{90}Pt-^{10}Ir and ^{90}Pt-^{10}Rh)[29]. Of these, the PGMs, especially platinum and iridium, occupied a particular place owing to their electrochemical inertness

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[27] Dreyman, E.W. (1972) Selection of anode materials. *Eng. Exp. Stn. Bull.* (West Virginia University), **106**, 76–83.

[28] Cailleret, L.; Collardeau, E. (1894) *C.R. Acad. Sci.*, **830**.

[29] Howe, J.L. (ed.) (1949) *Bibliography of the Platinum Metals 1931–1940*. Baker, Newark, NJ.

and intrinsic electrocatalytic activity. Actually, platinum is the most appropriate anode material for the preparation of persulfates, perchlorates, and periodates and for the regeneration of cerium (IV). However, the extremely high price of the bulk metal, which reached 1100 US$/oz. in early 2006, combined with its density (21,450 kg.m^{-3}), has drastically restricted its industrial uses. However, early in the century there was an attempt to develop an inert anode for oxygen evolution in sulfuric-acid-based electrolytes. The anode was obtained by coating a cheaper base metal with a thin layer of platinum or iridium. These first composite electrodes were patented in 1913 by Stevens.[30,31] The thin platinum or iridium layers were electroplated onto a refractory metal such as tungsten or tantalum. The role of the platinum coating was to insure the electrical conduction of the base metal, even under anodic polarization. Despite its novelty, this bright idea was not industrially developed at that time because it was impossible commercially to obtain these refractory metals, especially their mill products (e.g., plates, rods, sheet, and strips) needed for manufacturing large size industrial anodes. It was not until the 1960s that the first commercial platinized anodes appeared.

Besides the precious-metal anodes, early electrochemists used anodes made of two inexpensive materials such as lead and carbon-based materials such as graphite. The lead and the graphite were actually the only cheap anode materials that were industrially used up to the 1960s.

9.7.3.2.2 Lead and Lead-Alloy Anodes

Historically, the use of lead anodes resulted first from the widespread use of lead vessels in industrial manufacturing involving corrosive media such as the synthesis of sulfuric acid[32] and later from the original studies in the lead-acid battery invented by Gaston Planté in 1859.[33]

Properties. Lead is a common and cheap metal, and the average price for lead of 99.99 wt.% purity is 0.980 US$/kg.[34] Pure lead exhibits several attractive features, such as good electronic conductivity (20.64 μΩ.cm) and a good chemical and electrochemical corrosion resistance in numerous corrosive and oxidizing environments (e.g., chromates, sulfates, carbonates, and phosphates).[35] This chemical and electrochemical inertness is due to the self-formation of a protective passivating layer. For instance, the corrosion rate of the pure metal in 50 wt.% sulfuric acid is 130 μm per year at 25°C. When the metal undergoes an anodic current density of 1 kA.m^{-2} in 60 wt.% sulfuric acid, the corrosion rate reaches only 9 mm per year.[36,37] In fact, Pavlov[38] has shown in acidic sulfate electrolytes that, with an increasing anodic polarization, first an insulating layer of ***anglesite*** ($PbSO_4$) forms between 1.52 and 1.72 V/SHE, then a brown colored layer of semiconductive lead dioxide (PbO_2) appears. If anodic polarization is increased further, an insulating film of PbO forms, preventing the current from flowing. The lead anode is characterized by a high anodic overpotential for the evolution of oxygen. It is important to note that among the dimorphic forms of PbO_2 only the ***plattnerite*** with a rutile structure is electrocatalytic to oxygen evolution (cf. section on lead-dioxide anodes). Because

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[30] Stevens, R.H. (1913) Platinum-plated tungsten electrode. US Patent 1,077,894; November 4, 1913.

[31] Stevens, R.H. (1913) Iridium-plated tungsten electrode. US Patent 1,077,920; November 4, 1913.

[32] Lunge, G.; Naville, J. (1878) Traité de la grande industrie chimique. Tome I: acide sulfurique et oléum. Masson & Cie, Paris.

[33] Planté, G. (1859) *Compt. Rend. Acad. Sci.*, **49**, 221.

[34] Metal Bulletin Weekly, May 8, 2006.

[35] Greenwood, N.N.; Earnshaw, N. (1984) *Chemistry of the Elements*. Pergamon, Oxford, p. 435.

[36] Beck, F. (1971) Lead dioxide-coated titanium anodes. German Patent 2,023,292; May 13, 1971.

[37] Beck, F.; Csizi, G. (1971) Lead dioxide-titanium compound electrodes. German Patent 2,119,570; April 22, 1971.

[38] Pavlov, D.; Rogachev, T. (1986) Mechanism of the action of silver and arsenic on the anodic corrosion of lead and oxygen evolution at the lead/lead oxide (PbO_{2-x})/water/oxygen/sulfuric acid electrode system. *Electrochim. Acta.*, **31**(2), 241–249.

Table 9.17. Lead and lead-alloy-anode composition and electrochemical uses

Lead alloy [UNS numbers]	Typical composition range	Alloying effect	Electrochemical use
Pure lead (Pb) 'corroding lead' [L50000 – L50099]	>99.94 wt.% Pb	w/o	Nickel electrowinning (200 A.m^{-2})
Lead-silver (Pb-Ag) [L50100 – L50199]	0.25–0.80 wt.% Ag[39] (usually 0.5 wt.%)	Increases corrosion resistance and oxygen overvoltage	Zinc electrowinning Cobalt electrowinning
Lead-tin (Pb-Sn) [L54000 – L55099]	Usual 5–10 wt.% Sn Historically 4 wt.% Sn	Tin increases mechanical strength, forms corrosion-resistant intermetallics, and improves melt fluidity during anode casting	Cobalt electrowinning (500 A.m^{-2})
Antimonial lead (Pb-Sb)[40] (hard lead) [L52500 – L53799]	2–6 wt.% Sb	Antimony lowers oxygen overvoltage, increases stiffness, strength, and creep resistance, extends freezing range, and lowers the casting temperature	Cobalt electrowinning Copper electrowinning (200 A.m^{-2})
Lead-calcium-tin (Pb-Ca-Sn) ('nonantimonial' lead) [L50700 – L50899]	0.03–0.15 wt.% Ca	Calcium imparts corrosion resistance and minimizes O_2 and H_2 overpotentials, while Sn imparts stiffness	Copper electrowinning (500 A.m^{-2})

lead is malleable and ductile with a high density (11,350 kg.m^{-3}) and has a low melting point (327.5°C) and a high coefficient of linear thermal expansion (30×10^{-6} K^{-1}), it exhibits a severe creep phenomenon when electrolysis is conducted well above the ambient temperature. To improve the mechanical properties of pure lead and its corrosion properties, industrial lead anodes are typically made of lead alloys instead of pure lead metal. Moreover, the use of alloying elements usually decreases the melting temperature required to cast new anode slabs. Actually, castability determines the anode integrity, and the temperature interval between liquidus and solidus temperatures is still an important consideration for anode manufacturers.

Grades of pure lead and lead alloys used in industrial anodes. Pure lead grades are called ***corroding lead*** and *common lead*, both containing 99.94 wt.% min Pb, and ***chemical lead*** and ***acid-copper lead***, both containing 99.90 wt.% min Pb. Lead of higher specified purity (99.99 wt.% Pb) is also available in commercial quantities but rarely used as anodes. International specifications include ASTM B 29 in the USA for grades of pig lead including federal specification QQ-L-171, German standard DIN 1719, British specification BS 334, Canadian Standard CSA-HP2, and Australian Standard 1812. Corroding lead exhibits the outstanding corrosion resistance typical of lead and its alloys. Chemical lead is a refined lead with a residual copper content of 0.04 to 0.08 wt.% Cu, and a residual silver content of 0.002 to 0.02 wt.% Ag is particularly desirable in the chemical industries and thus is called chemical lead. Copper-bearing lead provides corrosion protection comparable to that of chemical lead in most applications that require high corrosion resistance. ***Common lead*** contains higher amounts of silver and bismuth than does corroding lead. In ***antimonial lead***, antimony content ranges

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[39] Hoffmann, W. (1962) *Blei und Bleilegierungen*. Springer, Berlin Heidelberg New York; English translation in 1962: *Lead and Lead Alloys*. Springer, Berlin Heidelberg New York.

[40] Mao, G.W.; Larson, J.G.; Rao, G.P. (1969) Effect on small additions of tin on some properties of lead 4.5 wt.% antimony alloys. *J. Inst. Metal*, **97**, 343–350.

from 0.5 to 25 wt.% Sb, but it is usually between 2 to 5 wt.% Sb. Antimony imparts greater hardness and strength. Lead-calcium alloys have replaced lead-antimony alloys in a number of applications. These alloys contain 0.03 to 0.15 wt.% Ca. More recently, aluminum has been added to calcium-lead and calcium-tin-lead alloys as a stabilizer for calcium. Adding tin to lead or lead alloys increases hardness and strength, but lead-tin alloys are more commonly used for their good melting, casting, and wetting properties. Tin gives an alloy the ability to wet and bond with metals such as steel and copper; unalloyed lead has poor wetting characteristics. The most common lead alloys used to manufacture industrial anodes together with their electrochemical applications are briefly summarized in Table 9.17.

Industrial applications. For those reasons, and despite its poor electrocatalytic properties and problems related to its toxicity arising with anodic dissolution, today lead anodes are the most common industrial anodes used worldwide for electrowinning metals from acidic sulfate electrolytes[41] (e.g., Zn, Co, Ni) and in hexavalent chromium electroplating.[42] The low price of lead anodes compared to titanium-coated electrodes and a service life in the range of 1 to 3 years are their major advantages. Moreover, the low melting temperature of lead and its alloys makes it possible to recycle in-house spent industrial lead anodes by simply remelting the discarded anodes and cast the recycled molten metal into new anode slabs. Zinc electrowinning uses lead-silver. Pb-Ag is the standard because cobalt addition cannot be used. The silver alloy imparts some corrosion resistance to the base lead. Lead-based anodes are used because of their low cost and robustness. But the major drawbacks are sludge generation leading to product quality issues and high oxygen overpotential, i.e., higher power costs. Copper electrowinning uses lead-calcium-tin. Lead-calcium-tin is favored to avoid the cost of silver addition. Stabilization of Pb-Ca-Sn anodes is ensured by the careful addition of cobalt (II) as depolarizer in the electrowinning electrolyte. In the electrolytic production of manganese metal, silver-lead anodes (1 wt.% Ag) are used in producing electrolytic metallic manganese, which results in anode sliming of 0.38 to 0.45 tonnes per tonne of Mn. Slime of manganese and lead compounds is a process waste that engenders a number of problems:

(i) environment pollution by waste products;
(ii) unproductive raw-material consumption, resulting in an increase in the overall volume of facilities and capital investments;
(iii) high specific energy consumption during preparation of additional quantities of manganese-containing solutions for electrolysis baths;
(iv) unpredictable anode destruction caused by active corrosion along waterlines;
(v) frequent cleanup of anodes and baths (once every 20 to 24 days), replacement of diaphragms, and remelting of anodes.

Recent developments. Some work is still being carried out to overcome some of the drawbacks of industrial lead anodes. For instance, the Japanese subsidiary of De Nora, Permelec Co., has developed a reinforced lead anode for the electrowinning of zinc from sulfate baths. This anode is made of a skin portion formed by a conventional silver-lead alloy and a stiffening reinforcing component made of titanium or zirconium mesh. The reduction in the thickness of the anodes, which is made possible by the provision of the reinforcing member, results in substantial savings in the amount of silver-bearing lead that is immobilized and a substantial reduction in the mass of the bulk anode. Later, Eltech Systems Corp. introduced its new patented technology,[43] known by the brand name Mesh-on-Lead™ (MOL)

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[41] De Nora, O. (1962) Anodes for use in the evolution of chlorine. British Patent 902,023; July 25, 1962.

[42] Nidola, A. (1995) Technologie di cromatura galvanica a spessore. *Rivista AIFM: Galvanotecnica e nuove finiture*, 5, 203–218.

[43] Brown, C.W.; Bishara, J.I.; Ernes, L.M.; Getsy, A.W.; Hardee, K.L.; Martin, B.L.; Pohto, G.R. (2002) Lead electrode structure having mesh surface. US Patent 6,352,622; March 5, 2002.

anode. The MOL anode is in fact a composite structure obtained by attaching disposable electrocatalytically active titanium mesh to existing lead anodes. Hence, it combines the benefits of a standard lead anode with power savings of a precious-metal-oxide-coated titanium found typically in dimensionally stable anodes (see DSA). The MOL product is still being developed to overcome its major drawback, cost. This new anode is specifically designated for replacing Pb-Ca-Sn anodes for primary copper electrowinning operations (e.g., SXEW process). The MOL concept was demonstrated with full-scale anodes at several premier commercial tankhouses. During these demonstrations MOL anodes exhibited numerous performance advantages relative to standard Pb-Ca-Sn anodes: they reduced specific energy consumption due to lower oxygen evolution overpotential, improved cathode quality, minimized lead-sludge generation, eliminated cobalt addition as a result of stabilized lead substrate, and improved current efficiency due to reduced short circuiting.[44]

Failure modes. In acidic sulfate baths, the most common failure mode of lead anodes consists of the formation of a thick solid and intermediate passivating layer of $PbSO_4$ and PbO_2 that can grow up to 5 mm thick and that eventually flakes off, leaving patches of freshly exposed surface. This deactivation of the lead anode is accompanied by two major drawbacks of industrial electrolysis: loss of faradic efficiency, usually below 90% for zinc and below 95% for cobalt, and an uneven and dendritic aspect of the electrodeposited metal usually contaminated by traces of lead. Another important failure mode occurs due to the deleterious effect of manganese (II) cations. Actually, the presence of manganous cations as impurities in many electrolyte streams may cause important secondary anodic reactions to occur. During the anodic process manganous cations Mn^{2+} may either react at the anode surface to form soluble permanganate species (MnO_4^-) or insoluble manganese dioxide (MnO_2) that passivates the anode surface and then impedes the proper evolution of oxygen. Eventually, flakes on the anode can detach as slime that contains oxides and/or sulfates, which are the major source of lead contamination in electrowinned cathodes. In copper electrowinning, Co (II) is often used as depolarizer for the oxygen evolution reaction. However, cobalt can not be used during zinc electrowinning because it affects the overall current efficiency.

9.7.3.2.3 Carbon Anodes

History. Carbon-based electrode materials (e.g., carbon, semigraphite, and graphite) have been used in various electrochemical technologies since the beginning of electrochemistry, including electroanalysis, energy storage devices, and electrosynthesis. For instance, due to its chemical inertness toward hydrochloric acid and hydrogen chloride, graphite was the early anode material selected for HCl electrolysis for producing chlorine gas.[45] This process, initially developed in Germany during World War II[46] by Holemann and Messner at IG Farben Industrie,[47,48] was continued in the 1950s by De Nora-Monsanto[49,50] and Hoechst-Uhde.[51,52]

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[44] Moats, M.; Hardee, K.; Brown, Jr., C. (2003) Mesh-on-Lead anodes for copper electrowinning. *JOM*, **55**(7), 46–48

[45] Isfort, H. (1985) State of the art after 20 years experience with industrial hydrochloric acid electrolysis. *DECHEMA Monographien,* **98**, 141–155.

[46] Gardiner, W.C. (1946) *Hydrochloric Acid Electrolysis at Wolfen.* Field Information Agency, Technical (FIAT) Report No. 832, US Office of Military Government for Germany.

[47] Gardiner, W.C. (1947) Hydrochloric acid electrolysis. *Chem. Eng.*, **54**(1), 100–101.

[48] Holemann, H. (1962) The hydrochloric acid electrolysis. *Chem. Ing. Techn.*, **34**, 371–376.

[49] Gallone, P.; Messner, G. (1965) Direct electrolysis of hydrochloric acid. *Electrochem. Technol.*, **3**(11–12), 321–326.

[50] Messner, G. (1966) Cells for the production of chlorine from hydrochloric acid. US Patent 3,236,760; February 22, 1966.

[51] Grosselfinger, F.B. (1964) New chlorine source: by-product hydrochloric acid. *Chem. Eng.*, **71**(19), 172–174.

[52] Donges, E.; Janson, H.G. (1966) *Chem. Ing. Techn.*, **38**, 443.

Structure. As a general rule, carbon-based materials have similar microstructures consisting of a planar network of a six-membered aromatic-forming layered structure with sp^2-hybridized carbon atoms trigonally bonded to one another. The crystallite size and extent of microstructural order can vary from material to material (i.e., edge-to-basal-plane ratio), which has important implications for electron-transfer kinetics.

Properties. Carbon-based electrodes are attractive because carbon is a cheap material with an excellent chemical inertness, and it is easy to machine and has a low bulk density (2260 $kg.m^{-3}$). Furthermore, there is a great diversity of commercially available products (e.g., graphite, pyrolytic, impervious, or glassy) and in several forms (e.g., fibers, cloths, blacks, powders, or reticulated). The graphite variety, despite its anisotropy, high electrical resistivity (1375 μΩ.cm), and extreme brittleness, was once widely used for the electrolysis of brines. Graphite is highly corrosion resistant to concentrated hydrochloric acid even at the high anodic potential required for producing chlorine. Corrosion is not detectable if the concentration of hydrochloric acid is always maintained above 20 wt.% HCl during electrolysis. Carbon anodes are also the only appropriate anode material in certain processes where no other materials exhibit both a low cost and a satisfactory corrosion resistance. Actually, several industrial electrolytic processes performed in molten-salt electrolytes continue to use carbon anodes; these processes are: the electrowinning of aluminum by the Hall–Heroult process, the electrolytic production of alkali metals (e.g., Na, Li) and alkali-earth metals (e.g., Be, Mg), and finally the electrolytic production of elemental fluorine. However, the use of carbon anodes in the chlor-alkali process for the production of chlorine gas has now been discontinued due to the replacement by modern and more efficient anodes. In fact, in the 1960s, the improvement of the chlor-alkali processes (e.g., mercury cathode cell and diaphragm cell) required great efforts in research and development. The research was essentially focused on improving graphite anodes, which had some serious drawbacks: first, the nondimensional stability of the carbon anodes during electrolysis led to continuous increases in the interelectrode gap, which caused an ohmic drop; second, it had a high chlorine evolution overpotential; and third, it had a very short service life (i.e., 6 to 24 months) due to the corrosion by the chlorine and the inescapable traces of oxygen, which formed chlorinated hydrocarbons and carbon dioxide. These efforts led to the birth of the third generation of industrial dimensionally stable anodes (*vide infra*).

Failure modes. Due to its lamellar structure, graphite severely corrodes due to the intercalation of anions between graphene planes such as sulfate or perchlorate during anodic discharge, while alkali-metal cations and ammonium intercalate when cathodically polarized leads to severe exfoliation of the electrode materials. The degradation of carbon-based materials depends on the electrolyte, the nature of the carbon materials, and the concentration of intercalating species. Once the graphite particles float on the electrolyte surface, they can lead to serious electrical continuity issues (i.e., short circuit), especially in molten-salt electrolytes that are denser than graphite.

9.7.3.2.4 Lead Dioxide (PbO_2)

Structure. Lead dioxide exhibits two polymorphic forms: (i) ***scrutinyite*** (α-PbO_2) with orthorhombic crystals (a = 497.1 pm, b = 595.6 pm, and c = 543.8 pm) with a density of 9867 $kg.m^{-3}$, and (ii) ***plattnerite*** (β-PbO_2) with tetragonal crystals (a = 495.25 pm and c = 338.63 pm) having a rutile-type structure and a density of 9564 $kg.m^{-3}$.

Properties. Only plattnerite has attractive features for electrochemical applications such as a low electrical resistivity (40 to 50 μΩ.cm), a good chemical and electrochemical corrosion resistance in sulfates media even at low pH, and a high overvoltage for the evolution of oxygen in sulfuric- and nitric-acid-containing electrolytes while it withstands chlorine evolution in hydrochloric acid. In fact, the more electrochemically active phase consists of a nonstoichiometric lead dioxide with the empirical chemical formula PbO_n (with $1.4 < n < 2$). A review of its preparation is presented by Thangappan et al.[53]

Preparation. Lead dioxide forms on pure lead, in dilute sulfuric acid, when polarized anodically at electrode potentials ranging from +1.5 to +1.8 V/SHE. Hence, industrially, lead-dioxide anodes are prepared by *in situ* anodization of a pure lead anode carried out at 20°C. The lead anode and a copper cathode are immersed in an undivided cell containing a dilute sulfuric acid (98 $g.dm^{-3}$ H_2SO_4) flowing with a rate ranging from 5 to 10 $dm^3.min^{-1}$, and the electrodeposition is conducted galvanostatically by applying an anodic current density of 100 $A.m^{-2}$ for 30 min. The inherent brittleness of the PbO_2 ceramic coating on soft lead can be overcome by electrodepositing anodically lead dioxide onto inert and stiff substrates such as titanium, niobium, tantalum, graphite, and Ebonex®. These supported anodes, that is, Ti/PbO_2 and Ta/PbO_2,[54] are now commercially available.[55,56] The anodic electrodeposition of a layer of PbO_2 is usually conducted in an undivided cell with a copper cathode and a stationary or flowing electrolyte consisting of dilute sulfuric acid (98 $g.dm^{-3}$ H_2SO_4) containing 1 $mol.dm^{-3}$ lead (II) nitrate with minute amounts of copper (II) or nickel (II) nitrate. Copper and nickel cations are used as cathodic depolarizers to impede the deleterious electrodeposition of lead on the cathode. Prior to coating, the metal substrate is first sandblasted to increase roughness and enhance the coating adhesion; this is followed by chemical etching. Etching is conducted, for instance, in boiling concentrated hydrochloric acid for titanium and its alloys or in cold concentrated hydrofluoric acid for niobium and tantalum. Etching removes the passivation layer that is always present on refractory metals. Then lead dioxide is electrodeposited galvanostatically at 200 $A.m^{-2}$ for several hours to reach anode loadings of several grams per square meter. The PbO_2 coating obtained is smooth, dense, hard, uniform, and free of pinholes and adheres to the surface of the substrate material. Sometimes a thin intermediate platinum layer is inserted between the base metal and the PbO_2 coating to enhance the service life by preventing the undermining process. Finally, for particular applications requiring bulk ceramic anodes, the electrodeposited lead dioxide can also be crushed, melted, and cast into intricate shapes.

Applications. PbO_2-based anodes are used for their inertness and low cost and when the oxidation should be carried out without the competitive evolution of oxygen. PbO_2 anodes were once used as a substitute for the conventional graphite and platinum electrodes for regenerating potassium dichromate and in the production of chlorates and perchlorates.[57] These anodes were also extensively used in hydrometallurgy as oxygen anodes for electroplating copper and zinc in sulfate baths[58,59,60] and in organic electrosynthesis for the production of glyoxilic acid from oxalic acid using sulfuric acid as supporting electrolyte.[61]

Failure modes. For lead dioxide supported on lead, the mismatch of strength and thermal expansion between the lead metal substrate and its lead-dioxide ceramic coating leads to flaking and spalling with loss of coating. As mentioned previously, a thin platinum underlayer can

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[53] Thangappan, R.; Nachippan, S.; Sampath, S. (1970) Lead dioxide-graphite electrode. *Ind. Eng. Chem. Prod. Res. Dev.*, **9**(4), 563–567.

[54] Pohl, J.P.; Richert, H. (1980) In: Trasatti, S. (ed.) *Electrodes of Conductive Metallic Oxides*, Part A. Elsevier, Amsterdam, Chap. 4, pp. 183–220.

[55] De Nora, O. (1962) Anodes for use in the evolution of chlorine. British Patent 902,023; July 25, 1962.

[56] Kuhn, A.T. (1976) The electrochemical evolution of oxygen on lead dioxide anodes. – *Chemistry & Industry*, **20**, 867–871.

[57] Grigger, J.C.; Miller, H.C.; Loomis, F.D. (1958) Lead dioxide anode for commercial use. *J. Electrochem. Soc.*, **105**, 100–102.

[58] Engelhardt, V.; Huth, M. (1909) Electrolytic recovery of zinc. US Patent 935,250; September 28, 1909.

[59] Gaunce, F.S. (1964) Treatment of lead or lead alloy electrodes. French Patent 1,419,356; November 26, 1964.

[60] Higley, L.W.; Dressel, W.M.; Cole, E.R. (1976) U.S. Bureau of Mines, Report No. R8111.

[61] Goodridge, F.; Lister, K.; Plimley, R.; Scott, K. (1980) Scale-up studies of the electrolytic reduction of oxalic to glyoxylic acid. *J. Appl. Electrochem.*, **10**(1), 55–60.

delay the catastrophic undermining process induced by the loss of coating, but usually the use of lead-dioxide-coated titanium anodes solves this issue but increases capital costs. Another failure mode occurs when manganese (II) cations are present that form insoluble manganese dioxide (MnO_2). Eventually, flakes on the anode can detach, entraining the coating and forming slimes at the bottom of the electrolyzer.

9.7.3.2.5 Manganese Dioxide (MnO_2)

Manganese dioxide was used for a long time following the work of Huth,[62] where hard and dense anodes of MnO_2 were obtained by forming a main body of the MnO_2 anode and then repeatedly treating this body with $Mn(NO_3)_2$ and heating it to decompose the nitrate and form additional MnO_2. These anodes were once used extensively in hydrometallurgy for the electrowinning or electroplating of zinc,[63] copper, and finally nickel in sulfate baths. They are prepared by solution impregnation-calcination[64] or by anodization in a sulfuric solution containing manganous cations. However, they never have the same full expansion of lead dioxide owing to their high corrosion rate under extreme conditions, that is, at high temperature, high pH, and elevated anodic current density. Nevertheless, some improvements have been made to increase their stability. Feige prepared a supported Ti/MnO_2 anode made by sintering titanium and lead particles with MnO_2.[65] De Nora et al. obtained a Ti/MnO_2-type anode by the application of the classical painting-thermal decomposition procedure employed for the preparation of DSA®.[66]

9.7.3.2.6 Spinel (AB_2O_4)- and Perovskite (ABO_3)-Type Oxides

Structure. It is well known that some ceramic oxides of the inner transition metals (e.g., Mn, Fe, Co, and Ni) with a spinel-type structure ($A^{II}B^{III}{}_2O_4$) or, to a lesser extent, a perovskite-type structure ($A^{II}B^{IV}O_3$) are electrical conductors with electrocatalytic activities when doped with Li, Ni, and Co. Moreover, being sufficiently stable in corrosive electrolytes, they were developed as good candidates for the development of oxygen-evolving electrodes. Spinels are oxides with the general formula ${}^{IV}(A_{1-x}B_x)^{VI}(A_xB_{2-x})O_4$, where the divalent cations are denoted A = Mg^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, and Zn^{2+} and trivalent cations B = Al^{3+}, Fe^{3+}, Cr^{3+}, and V^{3+}. Hence two types of spinel structure must be distinguished: normal spinels with $x = 0$, meaning that all the divalent cations occupy tetrahedral sites, and inverse spinels with $x = 1$. Of these, rods of pure magnetite (Fe_3O_4) or its doped form[67] obtained by casting molten iron oxides have been used as industrial anodes since 1870. Apart from magnetite and ferrites, today other classes of spinels have been investigated such as cobaltites and chromites. Due to their better electrocatalytic properties and fewer health and safety issues, cobaltites (e.g., MCo_2O_4 with M= Mg, Cu, and Zn) are now preferred and are the only ones being developed.

Properties. These anodes, despite their good chemical inertness and electrochemical stability under high positive potential,[68,69] have nevertheless two main drawbacks: they are

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[62] Huth, M. (1919) Anodes of solid manganese peroxide. US Patent 1,296,188; March 4, 1919.

[63] Bennett, J.E.; O'Leary, K.J. (1973) Oxygen anodes. US Patent 3,775,284; November 27, 1973.

[64] Ohzawa, K.; Shimizu, K.; Takasue, T. (1967) Insoluble electrode for electrolysis. US Patent 3,616,302; February 27, 1967.

[65] Feige, N.G. (1974) Method for producing a coated anode. US Patent 3,855,084; December 17, 1974.

[66] De Nora, O.; Nidola, O.; Spaziante, P.M. (1978) Manganese dioxide electrodes. US Patent 4,072,586; February 7, 1978.

[67] Kuhn, A.T.; Wright, P.M. In: Kuhn, A.T. (ed.) (1971) *Industrial Electrochemical Processes*, Chap. 14. Elsevier, New York.

[68] Matsumura, Takashi; Itai, R.; Shibuya, M.; Ishi, G. (1968) Electrolytic manufacture of sodium chlorate with magnetite anodes. *Electrochem. Technol.*, **6**(11–12), 402–404.

[69] Itai, R.; Shibuya, M.; Matsumura, T.; Ishi, G. (1971) Electrical resistivity of magnetite anodes. *J. Electrochem. Soc.*, **118**(10), 1709–1711.

brittle, which means a ceramic must be supported on a stiff metal substrate, and they exhibit very high electrical resistivities (27,000 μΩ.cm) with respect to other electrode materials.

Preparation. These oxides are usually produced by firing metallic precursors (e.g., nitrates, oxalates) in a moderately oxidizing atmosphere (e.g., steam, or argon-carbon dioxide mixture) at moderate temperatures (700 to 900°C). For reinforcing a brittle ceramic, these oxides can be used supported on a stiff base metal such as titanium.[70] Sometimes, such as for PbO_2 anodes, an thin intermediate layer of platinum is deposited between the base metal and the magnetite to enhance the service life and delay the undermining process.

9.7.3.2.7 Ebonex®(Ti_4O_7 and Ti_5O_9)

Since 1983, the date of the original patent of Hayfield[71] from IMI (Marston) describing a novel semiconductive electrode material that was prepared from substoichiometric oxides of titanium. These ceramics have attracted particular attention in the electrochemical community.[72,73] Soon after, the intellectual property related to the suboxides of titanium was purchased by the company Ebonex Technologies Incorporated (ETI), which was itself a subsidiary of ICI (Americas) and commercialized under the trade name Ebonex®.[74] Later, in 1992, the company was renamed Atraverda Limited. Bulk ceramic electrodes are manufactured in various forms (e.g., plates, tubes, rods, honeycombs, fibers, powders, and pellets) and grades (e.g., vitreous and porous). From a crystallochemical point of view, these ceramics consist of substoichiometric oxides of titanium with the Andersson–Magnéli crystal lattice structure[75] and the general chemical formula Ti_nO_{2n-1}, where n is an integer equal to or greater than 4 (e.g.,Ti_4O_7, Ti_5O_9, Ti_6O_{11}, Ti_7O_{13}, Ti_8O_{15}, Ti_9O_{17}, and $Ti_{10}O_{19}$). They are usually prepared by thermal reduction at 1300°C of pure TiO_2 by hydrogen, methane, or carbon monoxide, or a blend of titanium dioxide and titanium metal powder. These oxides have all comparably elevated electronic conductivity similar, and in some cases superior, to that of graphite (e.g., 630 μΩ.cm for Ti_4O_7 compared with 1375 μΩ.cm for graphite). From a corrosion point of view, Ebonex® exhibits an unusual chemical inertness in several corrosive media such as strong, oxidizing, or reducing mineral acids (e.g., HCl, H_2SO_4, HNO_3, and even HF). The anomalous high resistance to HF, and fluoride anions that usually readily attack titania even in dilute solutions, seems due to the difference in the lattice structure and the absence of hydrates. Ebonex® has also served as substrate for electrodepositing with a platinum coating[76] and been used as a platinized anode.[77] These anodes show no major differences with bulk platinum anodes.

Moreover, Pletcher and coworkers succeeded in electroplating coatings of metals such as Cu, Au, Ni, Pd, and Pt without any pretreatment of the substrate. In addition, by contrast

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[70] Hayes, M.; Kuhn, A.T. (1978) The preparation and behavior of magnetite anodes. *J. Appl. Electrochem.*, **8**(4), 327–332.

[71] Hayfield, P.C.S. (1983) Electrode material, electrode and electrochemical cell. US Patent 4,422,917; December 27, 1983.

[72] Baez, V.B.; Graves, J.E.; Pletcher, D. (1992) The reduction of oxygen on titanium oxide electrodes. *J. Electroanal. Chem.*, **340**(1–2), 273–86.

[73] Graves, J.E.; Pletcher, D.; Clarke, R.L.; Walsch, F.C. (1991) The electrochemistry of Magneli phase titanium oxide ceramic electrodes. I. The deposition and properties of metal coatings. *J. Appl. Electrochem.*, **21**(10), 848–857.

[74] Clarke, R.; Pardoe, R. (1992) Applications of ebonex conductive ceramics in effluent treatment. In: Genders, D.; Weinberg, N. (eds.) *Electrochemistry for a Cleaner Environment.* Electrosynthesis Company, Amherst, NY, pp. 349–363.

[75] Andersson, S.; Collen, B.; Kuylienstierna, U.; Magneli, A. *Acta Chem. Scand.*, **11**, 1641.

[76] Farndon, E.E.; Pletcher, D.; Saraby-Reintjes, A. (1997) The electrodeposition of platinum onto a conducting ceramic, Ebonex. *Electrochimica Acta*, **42**(8), 1269–1279.

[77] Farndon, E.E.; Pletcher, D. (1997) Studies of platinized Ebonex electrodes. *Electrochimica Acta*, **42**(8), 1281–1285.

Table 9.18. Miscellaneous properties of Ebonex® (Source: Atraverda)

Properties (at room temperature unless otherwise specified)	Bulk ceramic	Composite with polymer
Density (ρ/kg.m^{-3})	3600–4300	2300–2700
Specific heat capacity (c_p/J.kg^{-1}K^{-1})	750	n.a.
Thermal conductivity (k/W.m^{-1}K^{-1})	10–20	n.a.
Coefficient of linear thermal expansion (α/10^{-6}K^{-1})	6	n.a.
Flexural strength (/MPa)	60–180	n.a.
Vickers microhardness (H_v)	230	n.a.
Electrical conductivity (κ/S.m^{-1})	3000–30,000	100–1000
Temperature range (T/°C)	Up to 250°C in air or 800°C (reducing)	Up to 250°C
Oxygen overpotential (V/SHE) in H_2SO_4 (1 mol.dm^{-3}) in NaOH (1 mol.dm^{-3})	 +1.75 +1.65	
Hydrogen overpotential (V/SHE) in H_2SO_4 (1 mol.dm^{-3}) in NaOH(1 mol.dm^{-3})	 –0.75 –0.60	

with titanium, which is highly sensitive to hydrogen embrittlement, Ebonex® has no tendency to form brittle titanium hydride in contact with nascent hydrogen evolved during cathodic polarization. From an electrochemical point of view, Ebonex® exhibits poor intrinsic electrocatalytic properties[78] and hence has high overpotentials for both hydrogen and oxygen evolution reactions[79] (e.g., oxygen starts to evolve at +2.2 V/SHE in 0.1M $HClO_4$).[80] This dual behavior allows Ebonex® to be used without restriction either as cathode or anode. Nevertheless, the use of the bare materials is limited under severe conditions such as high anodic current density due to the irreversible oxidation of Ti_4O_7 to insulating TiO_2. However, the overpotential of the Ebonex® material can be modified by the application of electrocatalysts (e.g., RuO_2, IrO_2) by the painting-thermal decomposition procedure employed for the preparation of DSA®. By contrast coated Ebonex® is capable of operating with traces of fluoride anions up to anodic current densities of 4 kA.m^{-2} in baths where DSA® failed rapidly by the undermining mechanism (e.g., conc. HCl, HF-HNO_3 mixtures, elevated fluoride content). Industrially, Ebonex® is recommended for several applications including, but not restricted to, the replacement of lead anodes in zinc electrowinning, for cathodic protection of steel reinforcing bars (i.e., rebars) in concrete, *in situ* electrochemical remediation of contaminated soils, in the purification of drinking water, in the treatment of waste effluents, and as bipolar electrodes in rechargeable batteries and even coated with PbO_2 for ozone generation.[81] The high cost of Ebonex®, combined with its brittleness, still limits its widespread uses.

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[78] Miller-Folk, R.R.; Noftle, R.E.; Pletcher, D. (1989) Electron transfer reactions at Ebonex ceramic electrodes. *J. Electroanal. Chem.*, **274**(1–2), 257–261.

[79] Pollock, R.J.; Houlihan, J.F.; Bain, A.N.; Coryea, B.S. (1984) Electrochemical properties of a new electrode material, titanium oxide (Ti_4O_7). *Mater. Res. Bull.*, **19**(1), 17–24.

[80] Park, S.-Y.; Mho, S.-I.; Chi, E.-O.; Kwon, Y.-U.; Yeo, I.-H. (1995) Characteristics of Ru and RuO_2 thin films on the conductive ceramics TiO and Ebonex (Ti_4O_7). *Bull. Kor. Chem. Soc.*, **16**(2), 82–84.

[81] Graves, J.E.; Pletcher, D.; Clarke, R.L.; Walsh, F.C. (1992) The electrochemistry of Magneli phase titanium oxide ceramic electrodes. II. Ozone generation at Ebonex and Ebonex/lead dioxide anodes. *J. Appl. Electrochem.*, **22**(3), 200–203.

9.7.3.2.8 Noble-Metal-Coated Titanium Anodes (NMCT)

During the 1950s and 1960s, at the peak of expansion of the American and Russian aircraft and space programs and with the development of nuclear power plants, industrial processes for the production of refractory metals (e.g., Ti, Zr, Hf, Nb, and Ta) reached commercial scale. These processes, like the Kroll process,[82] made reactive metals with a wide range of alloy compositions available for the first time. This development brought several advantages: a reduction in production costs, the standardization of alloy grades, and a great effort in R&D for using these metals beyond their original aircraft and nuclear applications. At this stage, all the difficulties associated with preparing anodes of refractory metals coated with precious metals vanished, and the idea invented 40 years ago by Stevens reappeared. Hence, niobium- and tantalum-platinized anodes were prepared following the works of Rhoda[83] and Rosenblatt[84] in 1955. In the latter patent, a layer of platinum was obtained on tantalum by the thermal decomposition of H_2PtCl_6 in an inert atmosphere. This thermal treatment, which was conducted between 800 and 1000°C, gave a thin interdiffusion layer of a few micrometers, consisting of an alloy between Ta and Pt. Furthermore, titanium, now commercially available due to the strong demand for turbine blades in aircraft engines, was studied both from a corrosion and electrochemical point of view at ICI by Cotton.[85,86] The study showed that the exceptional resistance of titanium to corrosion in seawater was due to the valve action property of its oxide, which allowed the metal to be protected under anodic polarization by an insulating layer of rutile (TiO_2). It is only in 1957 that Beer[87] at Magneto Chemie (The Netherlands) and Cotton[88,89] with the help of Angell at ICI (UK) showed independently but concurrently that attaching rhodium or platinum at the surface of titanium, either by electroplating or by spot welding, provided sufficient electrical conductivity to the base metal that it could be polarized anodically despite its passivation. It was assumed that anodic current passed through platinum or rhodium metal. These rhodized or platinized titanium bielectrodes were named ***noble metal coated titanium*** (NMCT). During the following decade, NMCTs were actively developed through a partnership between ICI and Magneto Chemie with the close contribution of other companies such as Inco, Engelhard,[90,91] and IMI-Kynock.[92] Other firms such as W.C. Heraeus,[93] Metallgeselschaft,[94] and Texas Instruments[95] have also worked independently on the subject. The best preparation procedure involves electroplating with platinum or rhodium because the electrodeposition allows for smooth and nonporous deposits with a good throwing power without requiring an expensive amount of platinum.[96]

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[82] Kroll, W.J. (1940) The production of ductile titanium. *Trans. Electrochem. Soc.*, **112**, 35–47.

[83] Rhoda, R.N. (1952) Electroless palladium plating. *Trans. Inst. Met. Finish.*, **36**(3), 82–85.

[84] Rosenblatt, E.F.; Cohn, J.G. (1955) Platinum-metal-coated tantalum anodes. US Patent 2,719,797; October 4, 1955.

[85] Cotton, J.B. (1958) Anodic polarization of titanium. *Chem. & Ind.*, **3**, 492–493.

[86] Cotton, J.B. (1958) The corrosion resistance of titanium. *Chem. Ind.*, **3**, 640–646.

[87] Beer, H.B. (1960) Precious-metal anode with a titanium core. British Patent 855,107; November 11, 1960.

[88] Cotton, J.B.; Williams, E.C.; Barber, A.H. (1957) Titanium electrodes plated with platinum-group metals for electrolytic processes and cathodic protection. Electrodes. British Patent 877,901; July 17, 1957.

[89] Cotton, J.B. (1958) Platinum-faced titanium for electrochemical anodes. A new electrode material for impressed current cathodic protection. *Platinum Metals Rev.*, **2**, 45–47.

[90] Haley, A.J.; Keith, C.D.; May, J.E. (1969) Two-layer metallic electrodes. US Patent 3,461,058.

[91] May, J.E.; Haley, A.J. (1970) Electroplating with auxiliary platinum-coated tungsten anodes. US Patent 3,505,178; April 7, 1970.

[92] Cotton, J.B.; Hayfield, P.C.S. (1965) Electrodes and methods of making same. British Patent 1,113,421; May 15, 1965.

[93] Muller, P.; Speidel, H. (1960) New forms of platinum-tantalum electrodes. *Metall.* **14**, 695–696.

[94] Schleicher, H.W. (1963) Electrodes for electrolytic processes. British Patent 941,177; November 6, 1963.

[95] Whiting, K.A. (1964) Cladding copper articles with niobium or tantalum and platinum outside. US Patent 3,156,976; November 17, 1964.

[96] Balko, E.N. (1991) *Electrochemical Applications of the Platinum Group: Metal Coated Anodes.* In: Hartley, F.R. (ed.) *Chemistry of the Platinum Group Metals: Recent Developments.* Elsevier, New York.

The electroplating baths contain a platinum salt such as the so-called P-salt, the hexachloroplatinic acid, or the sodium hexachloroplatinate (IV).[97] The electrocatalytic coating consists of platinum and rhodium present in their metallic forms. However, both rhodium and platinum have high chlorine overvoltage (e.g. 300 mV for Rh and 486 mV for Pt at 10 $kA.m^{-2}$) and exhibit a slight corrosion with the rate depending on the electrolyte and the nature of bath impurities (e.g., Cl^-, F^-, organics).

9.7.3.2.9 Platinized Titanium and Niobium Anodes (70/30 Pt/Ir)

The improvement of the noble-metal-coated-titanium anodes was the starting point of the study and preparation of ***platinized titanium anodes*** by the thermal decomposition of a precursor with the pioneering work of, for example, Angell and Deriaz, both from ICI.[98,99] The precursor consisted of a given mixture of hexachloroplatinic (H_2PtCl_6) and hexachloroiridic acids (H_2IrCl_6) dissolved in an appropriate organic solvent (e.g., linalool, isopropanol, or ethyl acetoacetate). Prior to applying the painting solution, the titanium substrate was thoroughly sandblasted to increase roughness and chemically etched to remove the passivating layer. Etchants included various chemicals such as hot concentrated hydrochloric acid, hot 10 wt.% oxalic acid, and hot 30 wt.% sulfuric acid. After each application the treated piece underwent a long thermal treatment at high temperature in air between 400 and 500°C. At that temperature thermal oxidation of the underlying titanium substrate is negligible. This original protocol was inspired by Taylor's works[100] used in the 1930s to obtain reflective coatings of Pt on glass for the manufacture of optical mirrors. The study of the thermal decomposition of these particular painting solutions was conducted by Hopper[101] in 1923 and more recently by Kuo[102] in 1974. Other companies interested in platinized titanium anodes prepared by thermal decomposition were Engelhard[103] and Ionics.[104] After long-term trials, the formulation and procedure were finally optimized. These anodes were initially commercialized in 1968 by IMI (Marston) under the trade name **K-type®** or **70/30 Pt/Ir.**[105] For optimum performance, the commercially pure titanium must be from ASTM grade 1 or 2 with equiaxed grain sizes ranging between 30 and 50 μm. The electrocatalytic coating consists of platinum and rhodium present in their metallic forms either as separate phases or as platinum-iridium intermetallic. In fact, after thermal decomposition titanium is coated with a highly divided mixture of metal oxides consisting essentially of 70 wt.% PtO_x to 30 wt.% IrO_x. The common anode loading is 10 $g.m^{-2}$. Later, Millington[106] observed that niobium, tantalum, and even tungsten[107] could also be used as substrates, but they were only considered by certain suppliers[108] when titanium showed deficiencies owing to their greater cost. These anodes were rapidly used in numerous processes requiring a long service life under severe conditions. For example, they were

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[97] Lowenheim, F.A. (1974) *Modern Electroplating*, 3rd ed. Wiley, New York.

[98] Angell, C.H.; Deriaz, M.G. (1961) Improvements in or relating to a method for the production of assemblies comprising titanium. British Patent 885,819; December 28, 1961.

[99] Angell, C.H.; Deriaz, M.G. (1965) Improvements in or relating to a method for the production of assemblies comprising titanium. British Patent 984,973; March 3, 1965.

[100] Taylor, J.F. (1929) *J. Opt. Soc. Am.*, **18**, 138.

[101] Hopper, R.T. (1923) *Ceram. Ind.* (June).

[102] Kuo, C.Y. (1974) Electrical applications of thin-films produced by metallo-organic deposition. – *Solid State Technol.* **17**(2), 49–55.

[103] Anderson, E.P. (1961) Method for preparing anodes for cathodic protection systems. US Patent 2,998,359; August 29, 1961.

[104] Tirrel, C.E. (1964) Method for making non corroding electrode. US Patent 3,117,023; January 7, 1964.

[105] Hayfield, P.C.S.; Jacob, W.R. (1980) In: Coulter, M.O. (ed.) *Modern Chlor-Alkali Technology*. Ellis Horwood, London, Chap. 9, pp. 103–120.

[106] Millington, J.P. (1974) Lead dioxide electrode. British Patent 1,373,611; November 13, 1974.

[107] May, J.E.; Haley, Jr., A.J. (1970) Electroplating with auxiliary platinum-coated tungsten anodes. US Patent 3,505,178; April 7, 1970.

[108] Haley, Jr., A.J. (1967) *Engelhardt Ind. Tech. Bull.*, **7**, 157.

employed for the cathodic protection of immersed plants such as oil rigs, storage tanks, and subterranean pipe-lines,[109,110] in the electrolytic processes for the production of sodium hypochlorite,[111] electrodialysis, for regeneration of Ce(IV) in perchloric or nitric acid,[112] and for oxidation of sulfuric acid in peroxodisulfuric acid.[113] It is interesting to note that De Nora registered a patent on a Pt-coated anode in which the base metal was a ferrosilicon with some amounts of chromium.[114] Other formulations consisted of clad platinum metal on a copper-clad titanium or niobium core by roll bonding or a sandwich of platinum-titanium (or niobium)-copper. This technique, which provides a thick, dense, and impervious platinum coating, is now commercialized by Anomet in the USA for the cathodic protection of oil rigs. This continuous research effort, always developed under pressure from industry, resulted in the 1960s in a new generation of anodes that are still widely used in all electrochemical fields and are discussed below. Nevertheless, although platinized titanium electrodes were found active, they still were found to be unsatisfactory for chlorine production. It was for this reason that Beer patented a new type of anode, discussed in the next section.

9.7.3.2.10 Dimensionally Stable Anodes (DSA®) for Chlorine Evolution

In the 1960s, Henri Bernard Beer, who worked at Permelec[115]and the Italian team of Bianchi, Vittorio De Nora, Gallone, and Nidola, started studying the electrocatalytic behavior of mixed metal oxides and nitride coatings for the evolution of chlorine and oxygen.[116,117] These oxides were obtained by the calcination of precursors but in an oxidizing atmosphere (i.e., air or pure oxygen). These RuO_2-based anodes or so-called "ruthenized titanium anodes," composed of mixed metal oxides (TiO_2-RuO_2) coated on a titanium metal, have been developed with great success since 1965, the year of Beer's famous patent.[118] At this stage, the selection of ruthenium was made only based on the low cost of the metal and its commercial availability. These electrodes were later protected by several patents.[119,120,121,122] It was the birth of the ***activated titanium anode*** (ATA), also called ***oxide-coated titanium anode*** (OCTA), designation now obsolete and modernized in the 1990 to ***mixed metal oxides*** (MMO). These anodes are characterized by a geometrical stability and a constant potential over a long time (more than 2 to 3 years). It is this dimensional stability in comparison with the graphite anodes that gives it its actual trade name: ***dimensionally stable anodes*** (the acronym DSA® is

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[109] Cotton, J.B.; Williams, E.C.; Barber, A.H. (1961) Improvements relating to electrodes and uses thereof. British Patent 877,901; September 20, 1961.

[110] Anderson, E.P. (1961) Method for preparing anodes for cathodic protection systems. US Patent 2,998,359; August 29, 1961.

[111] Adamson, A.F.; Lever, B.G.; Stones, W.F. (1963) *J. Appl. Chem.*, **13**, 483.

[112] Ibl, N.; Kramer, R.; Ponto, L.; Robertson, P.M. (1979) *Electroorganic Synthesis Technology. AIChE Symposium Series* No. 185 75, 45.

[113] Rakov, A.A.; Veselovskii, V.I.; Kasatkin, E.V.; Potapova, G.F.; Sviridon, V.V. (1977) *Zh. Prikl. Khim.* **50**, 334.

[114] Bianchi, G.; Gallone, P.; Nidola, A.E. (1970) Composite anodes. US Patent 3,491,014; January 20, 1970.

[115] Beer, H.B. (1963) Noble metal coated titanium electrode and method for making and using it. US Patent 3,096,272; July 2, 1963.

[116] Bianchi, G.; De Nora, V.; Gallone, P.; Nidola, A. (1971) Titanium or tantalum base electrodes with applied titanium or tantalum oxide face activated with noble metals or noble metal oxides. US Patent 3,616,445; October 26, 1971.

[117] Bianchi, G.; De Nora, V.; Gallone, P.; Nidola, A. (1976) Valve metal electrode with valve metal oxide semi-conductive face. US Patent 3,948,751; April 6, 1976.

[118] Beer, H.B. (1966) Electrode and method for making the same. US Patent 3,234,110; February 8, 1966.

[119] Beer, H.B. (1966) Method of chemically plating base layers with precious metals of the platinum group. US Patent 3,265,526; August 9, 1966.

[120] Beer, H.B. (1972) Electrode and coating therefor. US Patent 3,632,498; January 4, 1972.

[121] Beer, H.B. (1973) Electrode having a platinum metal oxide. US Patent 3,711,385; January 13, 1973.

[122] Beer, H.B. (1973) Electrode and coating therefor. US Patent 3,751,291; August 7, 1973.

a trademark of Electronor Corp.). The classical composition of the composite anodes is defined in Table 9.19 as follows[123]:

Table 9.19. Definition of dimensionally stable anodes

A dimensionally stable anode is a composite electrode made of:	(1) Base metal or substrate	A base metal with a valve action property, such as the refractory metals (e.g., Ti, Zr, Hf, Nb, Ta, Mo, W) or their alloys (e.g., Ti-0.2Pd, Ti-Ru). This base metal acts as a current collector.[124] Sometimes it is possible to find in the claims of some particular patents unusual base materials (e.g., Al, Si-cast iron, Bi, C, Ti_4O_7, Fe_3O_4).
	(2) Protective passivating layer	A thin and impervious layer (a few micrometers thick) of a protective valve metal oxide (e.g., TiO_2, ZrO_2, HfO_2, Nb_2O_5, Ta_2O_5, NbO_2 and TaO_2).
	(3) Electrocatalyst	An electrocatalytic oxide of a noble metal or, more often, an oxide of the PGMs. This PGM oxide (e.g., RuO_2, PtO_x, IrO_2) increases the electrical conductivity of the passivating film. Sometimes other oxides are added (e.g., SnO_2, Sb_2O_5, Bi_2O_3) and also carbides (e.g., B_4C) or nitrides.

As a general rule, these anodes are made from a titanium base metal covered by a rutile layer TiO_2 doped by RuO_2 (30 mol.%).[125,126] They were used extensively in the industry (e.g., De Nora, Magnetochemie, Permelec, Eltech Systems Corp., US Filter, and Heraeus) and today they are used in all chlor-alkali processes and in chlorate production.[127] The dimensionally stables anodes for chlorine evolution are described in the technical literature by the brand acronyms DSA®(RuO_2) and DSA®-Cl_2, and they enjoyed great success in industry for two reasons: first, ruthenium has the lowest price of all the PGMs and, second, its density is half that of its neighbors. Moreover, its electrocatalytic characteristics for the evolution of chlorine are satisfactory. In industrial conditions (2 to 4 $kA.m^{-2}$) the service life of these electrodes is over 5 years. Therefore, today, titanium is the only base metal used for manufacturing dimensionally stable anodes for chlorine evolution. The contribution of Beer's discovery to the development of industrial electrochemistry is very important. The reader can also find a complete story of the invention of DSA® as told by the inventor himself and written on the occasion of his receiving the *Electrochemical Society Medal*[128] award.

9.7.3.2.11 Dimensionally Stable Anodes (DSA®) for Oxygen

Several industrial processes require long-lasting anodes for evolving oxygen in an acidic medium. In comparison with the chlorine-evolution reaction, the evolution of oxygen leads

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[123] Nidola, A. In: Trasatti, S. (ed.) (1981) *Electrodes of Conductive Metallic Oxides. Part B*. Elsevier, Amsterdam, Chap. 11, pp. 627–659.

[124] De Nora, O.; Nidola, A.; Trisoglio, G.; Bianchi, G. (1973) British Patent 1,399,576.

[125] Vercesi, G.P.; Rolewicz, J.; Comninellis, C.; Hinden, J. (1991) Characterization of dimensionally stable anodes DSA-type oxygen evolving electrodes. Choice of base metal. *Thermochimica Acta*, **176**, 31–47.

[126] Comninellis, Ch.; Vercesi, G.P. (1991) Characterization of DSA-type oxygen evolving electrodes: choice of a coating. *J. Appl. Electrochem.*, **21**(4), 335–345.

[127] Gorodtskii, V.V.; Tomashpol'skii, Yu.Ya.; Gorbacheva, L.B.; Sadovskaya, N.V.; Percherkii, M.M.; Erdokimov, S.V.; Busse-Machukas, V.B.; Kubasov, V.L.; Losev, V.V. (1984) *Elektrokhimiya*, **20**, 1045.

[128] Beer, H.B. (1980) The invention and industrial development of metal anodes. *J. Electrochem. Soc.*, **127**, 303C–307C.

to higher positive potentials combined with an increase in the acidity leading to more severe conditions for the anode material. Hence most materials are put in their anodic dissolution or transpassive region. These conditions greatly restrict the selection of suitable materials. The only materials that withstand these conditions are gold and the PGMs, but their use is prohibited by their high densities and high prices when required in bulk. Today, when highly valuated chemicals are produced, these metals can be cladded onto common base metals and polarized under low anodic current densities (1 $kA.m^{-2}$), while for more demanding conditions a hydrogen-diffusion anode must be used. Nevertheless, their high electrocatalytic activity dictates their use as electrocatalysts. As a general rule, the increasing electrochemical activity could be classified as follows: Ir>Ru>Pd>Rh>Pt>Au.[129] The carbon anodes, sometimes impregnated with a dispersion of PGMs, are now totally obsolete owing to their high oxygen overvoltage and a rapid failure during electrolysis. In fact, owing to their high porosity, an intercalation phenomenon occurs: the anions penetrate in the lattice and expand the structure, leading rapidly to spalling of the electrode.[130]

Therefore most electrode materials described previously fail rapidly when operating at high anodic current densities (e.g., 2 to 15 $kA.m^{-2}$) imposed by demanding electrochemical processes such as high-speed gold plating,[132] high-speed electrogalvanizing of steel (e.g., Andritz Ruthner A.G. technology),[133] and zinc electrowinning. Based on good results obtained with mixed metallic oxides (MMO) such as TiO_2-RuO_2 and Ta_2O_5-RuO_2 for the chlorine reaction and the huge success of DSA® in the chlor-alkali industry, these anodes were optimized for the oxygen-evolution reaction. Several compositions of electrocatalysts and base metals were then actively studied. Many metal oxides exhibiting both a good electronic conductivity, multivalence states, and a low redox potential for the higher oxide versus the lower oxide couple have been reported as promising electrocatalysts. The experimental values for the standard redox potentials of oxide couples are presented in Table 9.20.

These data show clearly that of the candidate electrocatalysts, Ir, Ru, Os, Ni, and Co have lower redox potentials than Rh, Pd, and Pt. Despite its excellent electrocatalytic activity, ruthenium dioxide (RuO_2) is readily oxidized at 1.39V/SHE to give off the volatile ruthenium

Table 9.20. Standard potentials for several oxide couples[131]

Higher/lower oxide couple	Standard electrode potential at 298.15 K (E/V vs. SHE)
IrO_2/Ir_2O_3	0.930
RuO_2/Ru_2O_3	0.940
OsO_2/OsO_4	1.00
NiO_2/Ni_2O_3	1.43
CoO_2/Co_2O_3	1.45
RhO_2/Rh_2O_3	1.73
PtO_3/PtO_2	2.00
PdO_3/PdO_2	2.03

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[129] Miles, M.H.; Thomason, J. (1976) Periodic variations of overvoltages for water electrolysis in acid solutions from cyclic voltammetric studies. *J. Electrochem. Soc.*, **123**(10), 1459–1461.

[130] Jasinski, R.; Brilmyer, G.; Helland, L. (1983) Stabilization of glassy carbon electrodes. *J. Electrochem. Soc.*, **130**(7), 1634.

[131] Tseung, A.C.C.; Jasem, S. (1977) Oxygen evolution on semiconducting oxides. *Electrochim. Acta,* **22**, 31

[132] Smith, C.G.; Okinaka, Y. (1983) High speed gold plating: anodic bath degradation and search for stable low polarization anodes. *J. Electrochem. Soc.*, **130**, 2149–2157.

[133] Hampel, J. (1984) Process and apparatus for the continuous electroplating of one or both sides of a metal strip. US Patent 4,469,565; February 22, 1984.

tetroxide (RuO_4),[134] and it is too sensitive to electrochemical dissolution.[135,136] Osmium was excluded owing to the formation of volatile (*b.p.* 130°C) and hazardous tetroxide (OsO_4), while nickel and cobalt oxides exhibit poor conductivity. Therefore, iridium dioxide (IrO_2) is the most stable and active electrocatalyst coating, especially when prepared by the thermal decomposition of iridium-chloride precursors (e.g., H_2IrCl_6, $IrCl_4$). Other studies demonstrated the important selection of the valve metal oxide (e.g., TiO_2, Nb_2O_5, and Ta_2O_5). De Nora showed that the best formulation was Ta_2O_5-IrO_2.[137] Later, Comninellis and coworkers optimized the composition preparing a coating containing 70 mol.% IrO_2.[138] This product was later developed commercially by Eltech System Corp. under the trade name TIR-2000®. These anodes have achieved operation in high-speed electrogalvanizing at current densities as high as 15 $kA.m^{-2}$ and with service lives exceeding 4300 h.[139] In contrast to the coating wear limiting anode life in chlorine, the complex corrosion-passivation mechanism of the substrate beneath the coating is typically the limiting factor for oxygen-evolving anodes. Indeed, during coating preparation the thermal stresses transform the electrocatalyst layer into a typical microcracked structure.[140] The gaps between grains facilitate the penetration of the corrosive electrolyte down to the base metal (i.e., undermining process).[141,142,143] According to Hine et al., by analogy with the anodic deactivation mechanism of PbO_2- and MnO_2-coated anodes,[144] the failure mode involves the damage of the interface between the electrocatalyst and the base metal, forming a thin layer of insulating rutile. This insulating film decreases the anode active surface area, increasing the local anodic current density. This behavior ends up with the spalling of the coating. The deactivation can be easily monitored industrially because the operating cell voltage increases continuously up to the limiting potential delivered by the rectifier. At this stage the anode is considered to be deactivated and is returned to the supplier to be refurbished. The costly electrocatalyst coating is then removed from the substrate by chemical stripping. The etching operation is usually performed in a molten mixture of alkali-metal hydroxides (e.g., NaOH) containing small amounts of an oxidizing salt.[145] The precious catalyst is then recovered in the slimes at the bottom of the vessel, while the clean substrate is treated and reactivated by the classical procedure. Usually, the critical parameters that influence the service life of the anode are the anodic current density, the coating preparation, and impurities. Actually, several inorganic and organic pollutants can lead to the dissolution of titanium (e.g., fluoride anions[146]), scaling (e.g., manganous cations), and the loss of coating (e.g. organic acids, nitroalcohols, etc.). For example, in organic electrosynthesis, the service life of these electrodes ranges from

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[134] Hine, F.; Yasuda, M.; Noda, T.; Yoshida, T. ; Okuda, J. (1979) Electrochemical behavior of the oxide-coated metal anodes. *J. Electrochem. Soc.*, **126**(9), 1439–1445.

[135] Manoharan, R.; Goodenough, J.B. (1991) *Electrochim. Acta,* **36**, 19.

[136] Yeo, R.S.; Orehotsky, J.; Visscher, W.; Srinivasan,S. (1981) Ruthenium-based mixed oxides as electrocatalysts for oxygen evolution in acid electrolytes. *J. Electrochem. Soc.,* **128**(9), 1900–19004.

[137] De Nora, O.; Bianchi, G.; Nidola, A.; Trisoglio, G. (1975) Anode for evolution of oxygen. US Patent 3,878,083.

[138] Comninellis, Ch.; Vercesi, G.P. (1991) Characterization of DSA-type oxygen evolving electrodes: choice of a coating. *J. Appl. Electrochem.*, **21**(4), 335–345.

[139] Hardee, K.L.; Mitchell, L.K. (1989) The influence of electrolyte parameters on the percent oxygen evolved from a chlorate cell. *J. Electrochem. Soc.*, **136**(11), 3314–3318.

[140] Kuznetzova, E.G.; Borisova, T.I.; Veselovskii, V.I. (1968) *Elektrokhimiya* **10**, 167.

[141] Warren, H.I., Wemsley, D., Seto, K. (1975) *Inst. Min. Met. Branch Meeting*, February 11, 1975, **53**.

[142] Seko, K. (1976) *Am. Chem. Soc. Centennial Meeting*, New York.

[143] Antler, M.; Butler, C.A. (1967) *J. Electrochem. Technol.*, **5**, 126.

[144] Hine, F.; Yasuda, M.; Yoshida, T.; Okuda, J. (1978) *ECS Meeting*, Seattle, May 15, Abstract 447.

[145] Colo, Z.J.; Hardee, K.L.; Carlson, R.C. (1992) Molten salt stripping of electrode coatings. US Patent 5,141,563; August 25, 1992.

[146] Fukuda, K.; Iwakura, C.; Tamura, H. (1980) Effect of heat treatment of titanium substrate on service life of titanium-supported iridia electrode in mixed aqueous solutions of sulfuric acid, ammonium sulfate, and ammonium fluoride. *Electrochim. Acta*, **25**(11), 1523–1525.

500 to 1000 h in molar sulfuric acid at 60°C.[147] Hence the high cost (10 to 30 k$.m^{-2}) forbids their industrial use in those conditions. In the late 1970s, as a consequence of work done on cathodically modified alloys initially conducted in the 1940s in the former Soviet Union by the Tomashov group, followed in the 1960s by Stern and Cotton[148] at ICI, there appeared a titanium-palladium alloy (i.e., ASTM grade 7) in which a small amount of palladium (0.12 to 0.25 wt.% Pd) greatly improved the corrosion resistance in reducing acids. Hence, several patents claimed a substrate made of Ti-Pd for preparing DSA® for oxygen. Nevertheless, despite a certain improvement, their limited service life led to the abandonment of several industrial projects. Moreover, Cardarelli and coworkers demonstrated that the service life of Ti/Ta_2O_5-IrO_2 anodes was affected by impurities in commercially pure titanium and by alloying elements in titanium alloys.[149] In addition, the influence of other reactive and refractory metals (i.e., Nb, Ta, Zr) as substrate on the service life has been studied, and it has been observed by Vercesi et al.[150] that the performance of tantalum-based anodes was better than that of titanium-based electrodes. This good behavior was due to the remarkable corrosion resistance of tantalum owing to the valve action property of its passivating and impervious film of anodically formed tantalum pentoxide. However, the development of a bulk tantalum-based electrode is not practical from the viewpoint of economics. Actually, the high price of tantalum (461 US$/kg) combined with its high density (16,654 kg.m^{-3}), in comparison with titanium metal (4540 kg.m^{-3}), which has a medium-range price (50 US$/kg), precludes any industrial applications. As a consequence, an anode of tantalum is 35 times more expensive than a titanium anode. Furthermore, owing to its high reactivity versus oxygen above 350°C, the preparation of tantalum anodes involves great difficulties during the thermal treatment required for the manufacture of electrodes. For these reasons, the tantalum anode does not enjoy widespread industrial use. To decrease the cost, a thin tantalum layer deposited onto a common base metal is a very attractive alternative. This idea appeared for the first time in 1968 in a patent[151] registered by the German company Farbenfabriken Bayer and also in 1974 proposed by Jeffes in a patent of Allbright & Wilson.[152] In this last patent a composite DSA®-Cl_2 was made from a steel plate coated with 500 µm of tantalum prepared by chemical vapor deposition. Then the tantalum was coated with RuO_2 (steel/Ta/RuO_2). Twenty years later, the anodes made according to this process were not industrially developed. However, in 1990, in a European patent[153] registered by ICI, Denton and Hayfield described the preparation of oxygen anodes made of a thin tantalum coating deposited onto a common base metal using several techniques. Finally, in 1993, Kumagai et al.[154] from DAIKI Engineering in Japan prepared an anode made of a thin intermediate layer of tantalum deposited onto a titanium base metal by sputtering (Ti/Ta/Ta_2O_5-IrO_2). To select the most optimized method for depositing tantalum onto a common substrate, a comprehensive comparison of tantalum coating techniques used in the chemical process industry was

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[147] Savall, A. (1992) Electrosynthèse organique. In: Électrochimie 92, *L'Actualité Chimique*, Special issue, January 1992.

[148] Potgieter, J.H.; Heyns, A.M.; Skinner, W. (1990) Cathodic modification as a means of improving the corrosion resistance of alloys. *J. Appl. Electrochem.*, **20**(5), 711–15.

[149] Cardarelli, F.; Comninellis, Ch.; Savall, A.; Taxil, P.; Manoli, G.; Leclerc, O. (1998) Preparation of oxygen evolving electrodes with long service life under extreme conditions. *J. Appl. Electrochem.*, **28**, 245.

[150] Vercesi, G.P.; Rolewicz, J.; Comninellis, C.; Hinden, J. (1991) Characterization of dimensionally stable anodes DSA-type oxygen evolving electrodes. Choice of base metal. *Thermochimica Acta*, **176**, 31–47.

[151] Farbenfabriken Bayer Aktiengesellschaft (1968) French Patent 1,516,524.

[152] Jeffes, J.H.E. (1974) Electrolysis of brine. British Patent 1,355,797; July 30, 1974.

[153] Denton, D.A.; Hayfield, P.C.S. (1990) Coated anode for an electrolytic process. European Patent 383,412; August22, 1990.

[154] Kumagai, N.; Jikihara, S.; Samata, Y.; Asami, K.; Hashimoto, A.M. (1993) The effect of sputter-deposited Ta intermediate layer on durability of IrO_2-coated Ti electrodes for oxygen evolution. In: *Proceeding of the 183rd Joint International Meeting of the Electrochemical Society,* 93–30(Corrosion, Electrochemistry, and Catalysis of Metastable Metals and Intermetallics), Abstract 324-33, Honolulu, HI, May 16-21, 1993.

recently reviewed by Cardarelli et al.[155] Moreover, the same authors developed anodes made from a thin tantalum layer deposited onto a common base metal (e.g. copper, nickel, or stainless steel) coated with an electrocatalytic mixture of oxides Ta_2O_5-IrO_2 produced by calcination. The performances of these anodes (stainless steel/Ta/IrO_2) are identical to that obtained with solid tantalum base metal (Ta/IrO_2).[156]

9.7.3.2.12 Synthetic Diamond Electrodes

Structure. The use of synthetic semiconductive diamond thin films in electrochemistry has only recently been reported.[157] Former designations such as diamondlike carbon (DLC) are now obsolete and so are not used in this book. By contrast with its other carbon allotropes, in diamond each carbon atom is tetrahedrally bonded to four other carbons using sp^3-hybrid orbitals.

Properties. Diamond has several attractive properties including the highest Young's modulus, thermal conductivity, and hardness of all solid materials, high electrical resistance, excellent chemical inertness, high electron and hole mobilities, and a wide optical transparency range (Section 12.5.1). The pure material is a wide bandgap insulator (E_g = 5.5 eV) and offers advantages for electronic applications under extreme environmental conditions. Nevertheless, when doped with boron, the material exhibits p-type semiconductive properties (i.e., IIb type diamond). Actually, doped diamond thin films can possess electronic conductivity ranging from that of an insulator at low doping levels to those of a good semiconductor for highly doped films (i.e., impurity level >10^{19} atoms.cm^{-3}). For instance, synthetic diamond thin films grown using hot-filament or microwave-assisted chemical vapor deposition can be doped to as high as 10,000 ppm at. of boron per carbon atom, resulting in films with resistivities of less than 10^5 μΩ.cm. Boron atoms that are electron acceptors form a band located roughly 0.35 eV above the valence band edge. At room temperature, some of the valence-band electrons are thermally promoted to this intermediate level, leaving free electrons in the dopant band and holes, or vacancies, in the valence band to support the flow of current. In addition, boron-doped diamond thin films commonly possess a rough, polycrystalline morphology with grain boundaries at the surface and a small-volume fraction of nondiamond carbon impurity. Hence, the electrical conductivity of the film surface and the bulk is influenced by the boron-doping level, the grain boundaries, and the impurities. Several interesting electrochemical properties distinguish boron-doped diamond thin films from conventional carbon-based electrodes. As a general rule, boron-doped diamond films exhibit voltammetric background currents and double-layer capacitances up to an order of magnitude lower than for glassy carbon. The residual or background current density in 0.1 M KCl measured by linear sweep voltammetry is less than 50 μA.cm^{-2} between −1.0 and +1.0 V/SHE. This indicates that the diamond-electrolyte interface is almost ideally polarizable. The evolution of hydrogen starts at roughly −1.75 V/SHE. The electrochemical span or working potential window, defined as the potentials at which the anodic and cathodic currents reach 250 μA.cm^{-2}, is 3.5 V for diamond compared to 2.5 V for glassy carbon. The overpotentials for hydrogen and oxygen evolution reactions are directly related to the nondiamond carbon impurity content. The higher the fraction of nondiamond carbon present, the lower the overpotentials for both these reactions. The double-layer capacitance for BDD in

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[155] Cardarelli, F.; Taxil, P.; Savall, A. (1996) Tantalum protective thin coating techniques for the chemical process industry: molten salts electrocoating as a new alternative. *Int. J. Refract. Metals Hard Mater.*, **14**, 365.

[156] Cardarelli, F.; Comninellis, Ch.; Leclerc, O.; Saval, A.; Taxil, P.; Manoli, G. (1997) Fabrication of an anode with enhanced durability and method for making the same. PCT International Patent Application WO 97/43465A1.

[157] Swain, G.; Ramesham, R. (1993) The electrochemical activity of boron-doped polycrystalline diamond thin film electrodes. Anal. Chem., 65(4), 345–351.

1 M KCl ranges from 4 to 8 μF.cm^{-2} over a 2-V potential window. There is a general trend toward increasing capacitance with more positive potentials, which is characteristic for p-type semiconductor electrode-electrolyte interfaces.[158] These capacitance values are comparable in magnitude to those observed for the basal plane of highly oriented pyrolytic graphite and significantly lower than those for glassy carbon (25 to 35 μF.cm^{-2}). The capacitance versus potential profile shape and magnitude for diamond is largely independent of the electrolyte composition and solution pH. On the other hand, boron-doped diamond electrodes have good electrochemical activity without any pretreatment.

Preparation. Diamond thin films can be prepared on a substrate from thermal decomposition of dilute mixtures of a hydrocarbon gas (e.g., methane) in hydrogen using one of several energy-assisted CVD methods, the most popular being hot-filament and microwave discharge.[159,160] The growth methods mainly differ in the manner in which the gas thermal activation is accomplished. Typical growth conditions are C/H ratios of 0.5 to 2 vol%, reduce pressures ranging from 1.33 to 13.3 kPa, a substrate temperature between 800 and 1000°C, and microwave powers of 1 to 1.3 kW, or filament temperatures of ca. 2100°C, depending on the method used. The film grows by nucleation at rates in the 0.1- to 1-μm/h range. For the substrates to be continuously coated with diamond, the nominal film thickness must be 1 μm. Wafer diameters of several centimeters can easily be coated in most modern reactors. Boron doping is accomplished from the gas phase by mixing a boron-containing gas such as diborane (B_2H_6) with the source gases, or from the solid state by gasifying a piece of hexagonal-boron nitride (h-BN).[161] Prior to deposition the substrate must be pretreated by cleaning it with a series of solvents, and nucleation sites are provided by embedding tiny diamond particles that are polished with a diamond paste. Hydrogen plays an important role in all of the growth methods as it prevents surface reconstruction from a saturated sp^3-hybridized diamond microstructure to an unsaturated sp^2-hybridized graphite microstructure; it also suppresses the formation of nondiamond carbon impurity, and it prevents several species from forming reactive radicals.

9.7.4 Electrodes for Corrosion Protection and Control

Apart from batteries, fuel cells, and industrial electrolyzers, corrosion protection and control is another field in which electrode materials occupy an important place.

9.7.4.1 Cathodes for Anodic Protection

Anodic protection[162] is a modern electrochemical technique for protecting metallic equipment used in the chemical-process industry against corrosion and handling highly corrosive chemicals (e.g., concentrated sulfuric and orthophosphoric acids). The technique consists in impressing a very low anodic current (i.e., usually 10 μA.m^{-2}) on a piece of metallic equipment (e.g., tanks, thermowells, columns) to protect against corrosion. This anodic polarization puts the electrochemical potential of the metal in the passivity region of its Pourbaix

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[158] Alehashem, S.; Chambers, F.; Strojek, J.W.; Swain, G.M.; Ramesham, R. (1995) New applications of diamond thin film technology in electro chemical systems. *Anal. Chem.*, **67**, 2812.

[159] Angus, J.C.; Hayman, C.C. (1988) Low-pressure, metastable growth of diamond and “diamondlike” phases. *Science* **241**, 913–921.

[160] Argoitia, A.; Angus, J.C.; Ma, J.S.; Wang, L.; Pirouz, P.; Lambrecht, W.R.L. (1994) Pseudomorphic stabilization of diamond on non-diamond substrates. *J. Mater. Res.*, **9**, 1849.

[161] Vinokur, N.; Miller, B.; Avyigal, Y.; Kalish, R. (1996) Electrochemical behavior of boron-doped diamond electrodes. *J. Electrochem. Soc.*, **143**(10), L238–L240.

[162] Riggs, Jr., O.L.; Locke, C.E. (1981) Anodic Protection: Theory and Practice in the Prevention of Corrosion. Plenum, New York.

diagram, i.e., where the dissolution reaction does not occur, and hence this leads to a negligible corrosion rate (i.e., less than 25 μm/year). The anodic protection method can only be used to protect metals and alloys exhibiting a passive state (e.g., reactive and refractory metals, stainless steels, etc.) against corrosion. Usually, the equipment required is a cathode, a reference electrode, or a power supply. The various cathode materials used in anodic protection are listed in Table 9.21.

Table 9.21. Cathode materials for anodic protection[163]

Cathode	Corrosive chemicals
Hastelloy®C	Nitrate aqueous solutions, sulfuric acid
Illium®G	Sulfuric acid (78–100 %wt.), oleum
Nickel-plated steel	Electroless nickel plating solutions
Platinized copper or brass	Acids
Silicon-cast iron (Duriron®) ASTM A518 grade 3	Sulfuric acid (89–100 %wt.), oleum
Stainless steels (AISI 304, 316L)	Nitrate aqueous solutions
Steel	Kraft digester liquid

9.7.4.2 Anodes for Cathodic Protection

Cathodic protection is the cathodic polarization of a metal to maintain its immunity in a corrosive environment. There are two ways to achieve an efficient cathodic polarization.

Table 9.22. Sacrificial anode materials[164]

Sacrificial anode material	Oxidation reaction	Electrode potential at 298.15 K (E_0/mV vs. SHE)	Capacity ($Ah.kg^{-1}$)	Consumption rate ($kg.A^{-1}.yr^{-1}$)	Notes
Magnesium	Mg^0/Mg^{2+}	−2360	1100	7.9	Buried soils, suitable for high-resistivity environments. Unsuited for marine applications due to high corrosion rate of magnesium in seawater
Zinc	Zn^0/Zn^{2+}	−760	810	10.7	Used in fresh, brackish, and marine water
Aluminum-Zinc-Mercury	Al^0/Al^{3+}	−1660	920–2600	3.0–3.2	Seawater, brines. Offshore and oil rigs, marine. Addition of In, Hg, and Sn prevent passivation
Aluminum-Zinc-Indium			1670–2400	3.6–5.2	
Aluminum-Zinc-Tin			2750–2840	3.4–9.4	

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[163] From Locke, C.E. (1992) *Anodic Protection*. In: *ASM Metals Handbook*, 10th ed. *Vol. 9. Corrosion,* ASM, Materials Park, OH, pp. 463–465.

[164] Dreyman, E.W. (1973) Selection of anode materials. *Eng. Exp. Stn. Bull.* (West Virginia University), **110**, 83–89.

The first is a passive protection that consists in connecting electrically the metal to a less noble material that will result in a galvanic coupling of the two materials, which leads to the anodic dissolution of the ***sacrificial anode***. The second method is an active protection that consists in using an impressed current power supply in order to polarize cathodically the workpiece versus a nonconsumable or inert anode.

Table 9.23. Impressed-current anode materials[165]

Sacrificial anode material	Composition	Typical anodic current density ($A.m^{-2}$)	Consumption rate ($g.A^{-1}.yr^{-1}$)	Cost per unit surface area (US$/$m^2$) 1-mm-thick anode	Notes
Dimensionally stable anodes (DSA®)	Ti/IrO_2 $Ti\text{-}Pd/IrO_2$ Nb/IrO_2 Ta/IrO_2	700 to 2000	Less than 1	9000 15,000 13,000 54,000	Cathodic protection of water tank and buried steel structures
Silicon-cast iron (Duriron®)	Fe-14.5Si-4.0Cr-0.8C-1.50Mn-0.5Cu-0.2Mo	10 to 40	200 to 500	500–1000	Both good corrosion and abrasion/wear resistance. Used extensively offshore, on oil rigs, and in other marine technology applications
Ebonex®	Ti_4O_7, Ti_5O_9	50 (naked) 2000 (IrO_2 coated)	n.a.	2000–3000	Corrosion resistant to both alkaline and acid media. Brittle and shock-sensitive material. Density 3600–4300 $kg.m^{-3}$. Conductivity 30–300 S/cm
Graphite and carbon	Carbon	10–40	225–450		Brittle and shock-sensitive materials. Used extensively buried for cathodic protection of ground pipelines
Lead-alloy anodes	$Pb\text{-}6Sb\text{-}1Ag/PbO_2$	160 to 220	45 to 90	15–20	Cathodic protection for equipment immersed in seawater
Platinized titanium (K-type 70/30)	$Ti/70PtO_x\text{-}30IrO_2$	500 to 1000	18	15,000	Low consumption rate, high anodic current, but expensive
Platinized niobium and tantalum anodes	Nb/Pt-Ir, Ta/Pt-Ir	500 to 1000	1 to 6	40,000–60,000	Low consumption rate, high anodic current, but expensive
Ebonex®/ Polymer composite	Ti_4O_7 with conductive polymer binder	n.a.	n.a.	1000	Cathodic protection of reinforced steel bars in salt-contaminated concrete. Density 2300–2700 $kg.m^{-3}$; conductivity 1–10 S/cm

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[165] Dreyman, E.W. (1973) Selection of anode materials. *Eng. Exp. Stn. Bull.* (West Virginia University), **110**, 83–89.

9.7.5 Electrode Suppliers and Manufacturers

Table 9.24. Industrial electrode manufacturers

Electrode supplier	Typical products and brand names	Contact address
Anomet Products	Pt/Nb/Cu, Pt/Ti/Cu	830 Boston Turnpike Road, Shrewsbury, MA 01545, USA Telephone: +1 (508) 842-3069 Fax: +1 (508) 842-0847 E-mail: info@anometproducts.com URL: http://www.anometproducts.com/
Anotec Industries	High silicon cast iron anodes for impressed current	5701 Production Way, Langley, V3N 4N5 British Columbia, Canada Telephone: +1 (604)514-1544 Fax: +1 (604) 514 1546 URL: http://www.anotec.com/
Atraverda Ltd. (formerly Ebonex Technology Inc.)	Andersson–Magnéli phases, Ti_4O_7, Ebonex®	Units A&B, Roseheyworth Business Park Abertillery, Gwent, NP13 1SX, UK Telephone:+44 (0) 1495 294 026 Fax:+44 (0) 1495 294 179 E-mail: info@atranova.com URL: http://www.atraverda.com
Chemapol Industries	Ti/RuO_2, Ti/IrO_2	Mumbai, India Telephone: +22 641 010 / 226 412 12 Fax: 22653636 E-mail: chemapol@rediffmail.comIndia
De Nora Elettrodi Spa	Ti/RuO_2, Ti/IrO_2, Nb/RuO_2, Ta/IrO_2	Via Bistolfi, 35, I-20134 Milan, Italy Telephone: (+39) 0221291 Fax: (+39) 022154873 E-mail: info@uhdenora.com URL: http://www.denora.it/
DISA Anodes	Ti/RuO_2, Ti/IrO_2, Nb/RuO_2, Ta/IrO_2	7 Berg Street, Jeppestown Johannesburg, Republic of South Africa Tel: +27 (0) 11 614 5238 / 5533 Fax: +27 (0) 11 614 0093 E-mail: lorenzo@disaanodes.co.za URL: http://www.disaeurope.it/products.html
Eltech Systems Corp.	DSA-Cl_2 and DSA-O_2 TIR®2000 MOL™	Corporate Headquarters 100 Seventh Avenue, Suite 300, Chardon, OH 44024, USA Telephone: +1 (440) 285-0300 Fax: +1 (440) 285-0302 E-mail: info@eltechsystems.com URL: http://www.eltechsystems.com/
Farwest Corrosion	Anodic, cathodic protection	1480 West Artesia Blvd., Gardena, CA 90248-3215, USA Telephone: +1 (310) 532-9524 Fax: +1 (310) 532-3934 E-mail: sales@farwestcorrosion.com
Magneto Special Anodes BV (formerly Magneto-chemie)	MMO, Ti/RuO_2, Ti/IrO_2, Nb/RuO_2, Ta/IrO_2	Calandstraat 109, NL-3125 BA Schiedam, Netherlands Telephone: (+31) 10-2620788 Fax: (+31) 10-2620201 E-mail: info@magneto.nl URL: http://www.magneto.nl

Table 9.24. *(continued)*

Electrode supplier	Typical products and brand names	Contact address
Permascand AB	MMO, Ti/RuO_2, Ti/IrO_2	P.O. Box 42, Ljungaverk, S-840 10, Sweden Telephone: (+46) 691 355 00 Fax: (+46) 691 331 30 E-mail: info@permascand.se URL: http://www.permascand.com
Ti Anode Fabricators P (TAF)	MMO, Ti/RuO_2, Ti/IrO_2	# 48, Noothanchery, Madambakkam, Chennai - 600 073, India Telephone: +91 44 2278 1149 Fax: +91 44 2278 1362 E-mail: info@tianode.com URL: http://www.tianode.com
Titanium Equipment & Anode Manufacturing Company (TEAM)	MMO, Ti/RuO_2, Ti/IrO_2	TEAM House, Grand Southern Trunk Road, Vandalur, Chennai - 600 048, India Telephone: + 91 44 2 2750323 / 24 Fax: + 91 44 2 2750860 E-mail: team@drraoholdings.com URL: http://www.team.co.in/
Titaninum Tantalum Products (TiTaN)	MMO, Ti/RuO_2, Ti/IrO_2, Nb/RuO_2, Ta/IrO_2	86/1, Vengaivasal Main Road Gowrivakkam, Chennai 601 302, Tamil Nadu, India Telephone: + 91 44 2278 1210 Fax: + 91 44 2278 0209 URL: http://www.titanindia.com/
US Filter Corp. (formerly Electrode Products)	MMO, Ti/RuO_2, Ti/IrO_2	2 Milltown Court, Union, NJ 07083, USA Telephone: +1 (908) 851-6921 Fax: +1 (908) 851-6906 E-mail: optimasales@usfilter.com URL: http://www.usfilter.com

9.8 Electrochemical Galvanic Series

Table 9.25. Galvanic series of metals and alloys in seawater

Metal or alloy
Corroded end (anodic or least noble)
Magnesium
Magnesium alloys
Zinc
Aluminum alloys 5052, 3004, 3003, 1100, 6053
Cadmium
Aluminum alloys 2117, 2017, 2024
Mild steel (AISI 1018), wrought iron
Cast iron, low-alloy high-strength steel
Chrome iron (active)
Stainless steel, AISI 430 series (active)
Stainless steels AISI 302, 303, 321, 347, 410, and 416(active)

Table 9.25. *(continued)*

Metal or alloy
Ni - Resist
Stainless steels AISI 316, 317 (active)
Carpenter 20Cb-3 (active)
Aluminum bronze (CA 687)
Hastelloy C (active), Inconel® 625 (active), titanium (active)
Lead-tin solders
Lead
Tin
Inconel® 600 (active)
Nickel (active)
60 Ni-15 Cr (active)
80 Ni-20 Cr (active)
Hastelloy® B (active)
Brasses
Copper (CDA102)
Manganese bronze (ca 675), tin bronze (ca903, 905)
Silicone bronze
Nickel silver
90Cu-10Ni
80Cu-20Ni
Stainless steel 430
Nickel, aluminum, bronze (ca 630, 632)
Monel 400 and K500
Silver solder
Nickel 200 (passive)
60Ni-15Cr (passive)
Inconel 600 (passive)
80Ni- 20Cr (passive)
Cr-Fe (passive)
Stainless steel grades 302, 303, 304, 321, 347 (passive)
Stainless steel grades 316 and 317 (passive)
Carpenter 20 Cb-3 (passive), Incoloy® 825 and Ni-Mo-Cr-Fe alloy (passive)
Silver
Titanium (pass.), Hastelloy® C276 (passive), Inconel® 625(pass.)
Graphite
Zirconium
Gold
Platinum
Protected end (cathodic or most noble)

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