United States Patent [19]

Graefen et al.

[11] **3,808,053**

[45]* **Apr. 30, 1974**

[54] **LEAD ALLOY FOR SOLID AND GRID ELECTRODES**

[75] Inventors: **Hubert Graefen,** Lampertheim; **Dieter Kuron,** Mannheim, both of Germany

[73] Assignee: **Badische Anilin- & Soda-Fabrik Aktiengesellschaft,** Ludwigshafen/Rhein, Land Rheinland-Pfalz, Germany

[*] Notice: The portion of the term of this patent subsequent to May 23, 1989, has been disclaimed.

[22] Filed: **Jan. 24, 1972**

[21] Appl. No.: **220,244**

[30] **Foreign Application Priority Data**

Jan. 27, 1971 Germany 2103689

[52] **U.S. Cl.** **136/26,** 75/166

[51] **Int. Cl.** **H01m 39/04**

[58] **Field of Search** 136/26; 75/166, 172

[56] **References Cited**

UNITED STATES PATENTS

2,418,710	4/1947	Hensel	75/172 A
3,664,831	5/1972	Graefen et al.	75/166 R
3,301,642	1/1967	Youssef	75/166 R

Primary Examiner—A. B. Curtis
Assistant Examiner—C. F. LeFevour
Attorney, Agent, or Firm—Johnston, Keil, Thompson & Shurtleff

[57] **ABSTRACT**

A lead alloy with 0.05 to 0.2 percent palladium as an electrode material for electrolytic plant and lead accumulators with improved corrosion behavior with respect to sulfuric acid and lower specific elongation and electrochemical attack.

3 Claims, 2 Drawing Figures

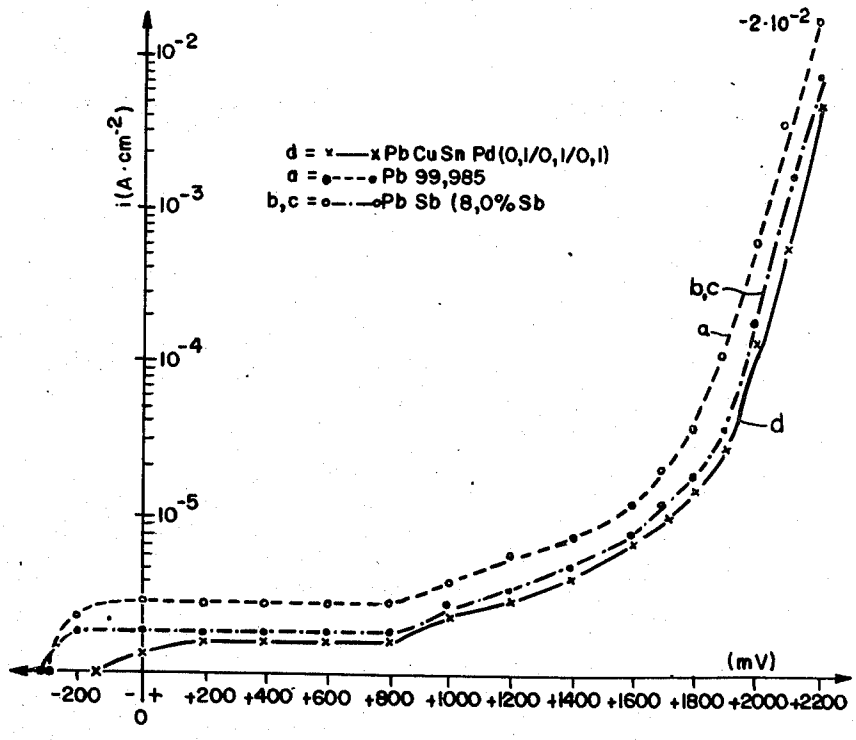


FIG. 2

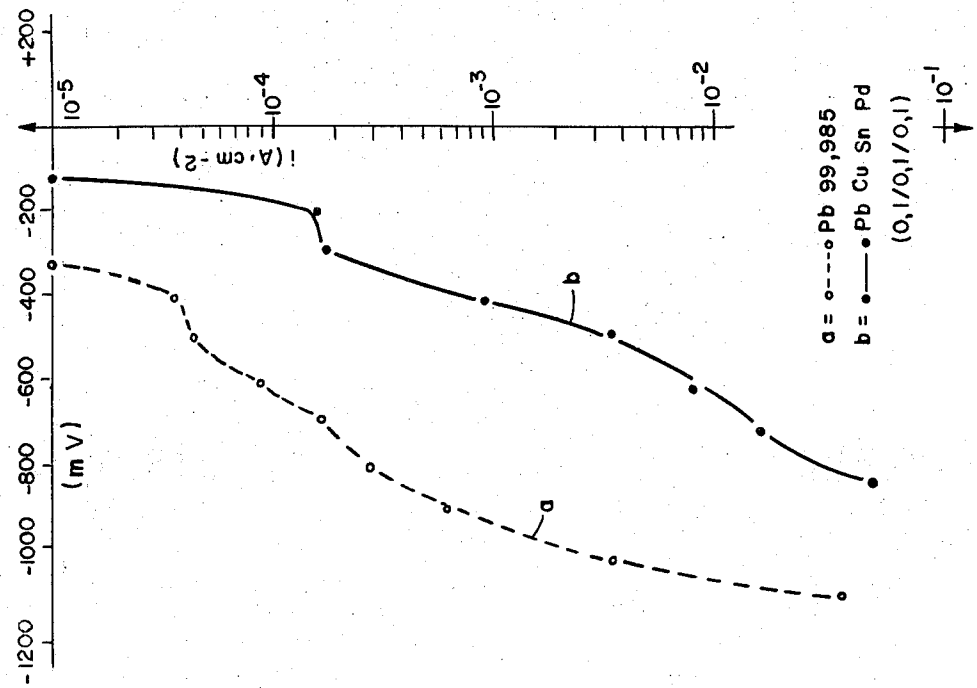
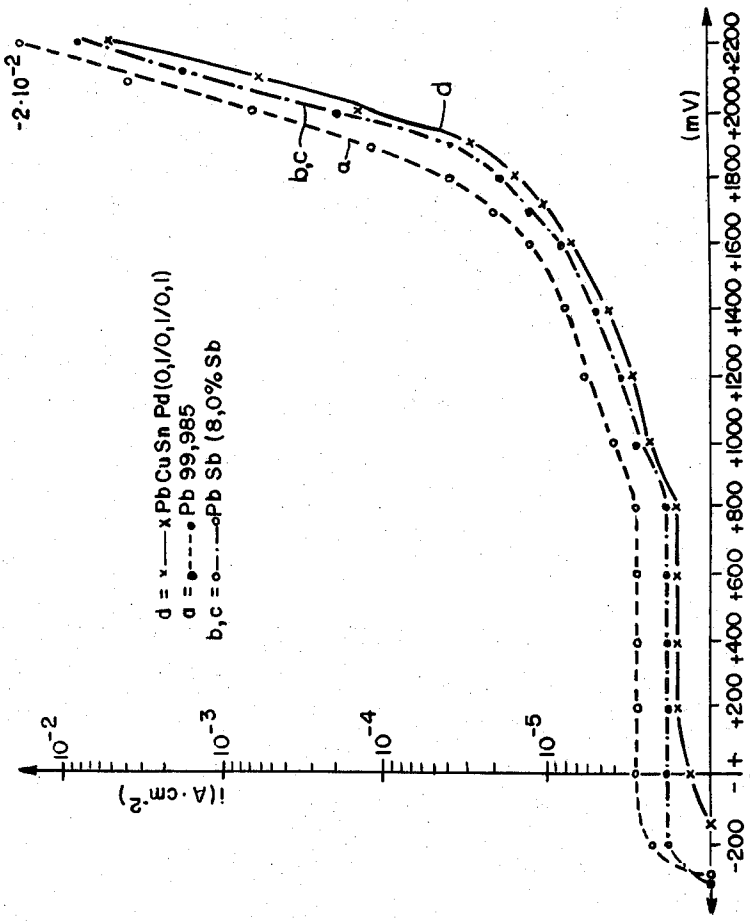

+200
-200
-400
-600
-800
-1000
-1200
(mV)
10^{-5}
10^{-4}
10^{-3}
10^{-2}
$i(A \cdot cm^{-2})$
a
b
a = o---o Pb 99,985
b = •——• Pb Cu Sn Pd
(0,1/0,1/0,1)
10^{-1}

FIG. 1


$-2 \cdot 10^{-2}$
b,c
a
d
(mV)
$i(A \cdot cm^{-2})$
10^{-2}
10^{-3}
10^{-4}
10^{-5}
0
-200
+200 +400 +600 +800 +1000 +1200 +1400 +1600 +1800 +2000 +2200
d = x——x Pb Cu Sn Pd (0,1/0,1/0,1)
a = •---• Pb 99,985
b,c = o-·-o Pb Sb (8,0% Sb

LEAD ALLOY FOR SOLID AND GRID ELECTRODES

The invention relates generally to lead alloys and in particular to the use of a lead alloy for solid and grid-type electrodes in electrolytic plant and lead accumulators.

The use of lead as electrode material for electrolytic plant is uneconomical in certain cases because of too marked corrosion in the case of cathodes.

The material for grid anodes in lead accumulators has hitherto generally been a hard lead alloy of varying composition, particularly one having antimony as a constituent. Grid anodes of conventional lead alloys exhibit wear and fatigue phenomena after a fairly short period of time and this markedly restricts the life of the accumulators. Some of these defects are for example corrosion, cathode poisoning by the antimony content, too low specific elongation and many others.

Lead alloys containing palladium (Pd) as a constituent are already known from our U.S. Pat. application Ser. No. 20,179 now U.S. Pat. No. 3,664,831. Palladium as an alloy component considerably increases corrosion resistance and mechanical strength, either alone or in conjunction with conventional alloy components for lead.

We have now found that electrode material based on lead and lead alloys for

a. electrochemical and electroplating plant and

b. lead accumulators

can be further improved in its efficiency and life when it contains palladium (Pd) as a component of the alloy. The use of an electrode of lead alloyed with palladium has proved to be superior to the use of lead alloys hitherto used, particularly as anodes for lead accumulators. The superiority and greater efficiency of such an electrode containing palladium as a component of the alloy is not lost when palladium is used in combination with other known alloy components for lead.

A lead alloy preferred according to the invention as an electrode material consists of 0.05 to 0.15 percent by weight of copper (Cu), 0.05 to 0.15 percent by weight of tin (Sn) and 0.05 to 0.2 percent by weight of palladium (Pd), the remainder being lead and the usual impurities.

The alloy according to the invention has improved resistance to corrosion by sulfuric acid which commends its use as an anode in the case of sulfuric acid as electrolyte generally and particularly as grid material for the anodes of accumulators.

Chemical attack values in mm/year of an alloy (d) according to this invention as compared with commercial fine lead (a) and two lead alloys (b) and (c) in sulfuric acid are given in the following Table. The materials used are:

a. Pb 99.985

b. PbSb (1.5% by weight)

c. PbSb (8% by weight)

d. PbCuSnPd (0.1%/0.1%/0.1% by weight)

Alloy	Without electrical load		With applied electrical potential	
	boiling 50% H_2SO_4	boiling 70% H_2SO_4	+3.4 volts 5% H_2SO_4 30°C	+2.1 volts Battery acid Rt
(a)	0.97	dissolved	8.0	0.1
(b)	0.41	3.80	13	
(c)	—	6.0	—	0.6
(d)	0.01	0.10	4.0	0.1

The curves of current density and potential in FIG. 1 illustrate these data and the improved efficiency.

The alloy according to this invention, because of its low hydrogen overvoltage, is also better than commercial lead and its alloys as an electrode material for cathodes. In this connection FIG. 2 shows the cathodic portions of current density/potential curves (a) of fine lead and (b) the alloy according to the invention in battery acid of a density of 1.26 g/ccm.

For the grids of the anodes of lead accumulators not only is good corrosion resistance desirable but also adequate strength and the lowest possible specific elongation. The alloy according to the invention satisfies these requirements and is therefore superior to the alloys previously used for the same purpose.

Comparative hardness data are collected in the following table:

Material	Hardness HB 2.5/3.1/120
Pb 99.985	3.6 kg/mm²
PbSb (8%)	6.4 kg/mm²
PbCuSnPd	6.5 kg/mm²

Specific elongation of the lead alloy proposed as an electrode material is also far below that of commercial lead and its known alloys even at elevated temperature. The 1 percent elongation limit is determined at a load of 0.3 kg/mm² at 23°C for a testing period of more than 10,000 hours and at 40°C for about 3,000 hours testing period. There is therefore a clear quantitative improvement against the active material falling out from the grid of an electrode made with the improved alloy.

The casting and processing properties of the alloy of the invention also satisfy the requirements for electrode materials based on conventional lead alloys.

We claim:

1. An article of manufacture comprising a grid electrode consisting essentially of 0.05 to 0.15 percent by weight of copper, 0.05 to 0.15 percent by weight of tin, and 0.05 to 0.2 percent by weight of palladium, the remainder being lead and the usual impurities.

2. An article of manufacture comprising a grid electrode serving as an anode for lead accumulators, said electrode consisting essentially of 0.05 to 0.15 percent by weight of copper, 0.05 to 0.15 percent by weight of tin, and 0.05 to 0.2 percent by weight of palladium, the remainder being lead and the usual impurities.

3. An article of manufacture comprising a grid electrode serving as an anode in electrolytic and electrochemical cells containing sulfuric acid as the anolyte, said electrode consisting essentially of 0.05 to 0.05 percent by weight of copper, 0.05 to 0.15 percent by weight of tin, and 0.05 to 0.2 percent by weight of palladium, the remainder being lead and the usual impurities.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,808,053 Dated April 30, 1974

Inventor(s) Hubert Graefen and Dieter Kuron

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, table at the bottom, "13" should read -- - --.

Signed and sealed this 7th day of January 1975.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.