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Effect of solidification temperature of lead alloy grids on the electrochemical behavior of lead-acid battery

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Abstract One of the main electrochemical characteristics of a lead-acid battery is amount of water consumption. The effect of solidification temperature on electrochemical behavior (mainly hydrogen overvoltage) of Pb–Ca–Sn–Al (0.09%, Ca; 0.9%, Sn; 0.02%, Al) and Pb–Sb–Sn (1.7%, Sb; 0.24%, Sn) alloys, which are used in making the grid of lead-acid batteries, has been studied by cyclic voltammetry (CV) and linear sweep voltammetry for different concentrations of sulfuric acid (ranging from 0.5 mol L⁻¹ to 4.0 mol L⁻¹). The morphology of the grid at some solidification temperatures was studied by optical microscopy. After one sweep of CV the surface of the electrode was investigated by using scanning electron microscopy. The results show that the potential of hydrogen evolution depends on the solidification temperature of the grids during production (mold temperature of grid casting). Also, at different solidification temperatures, different passivation phenomena, electrode surface constituents, and structure were observed.

Keywords Lead alloy · Mold temperature · Hydrogen overvoltage · Lead-acid battery

Introduction

Lead–antimony and lead–calcium alloys are most widely used for production of lead-acid battery grids. These alloys are extremely strong and creep-resistant and can be cast into rigid, dimensionally stable grids that are capable of resisting the stresses of charge/discharge reactions. As the antimony content of battery grids has been reduced, the mechanical properties of the alloys

have decreased significantly [1]. The SLI battery grids employed have about 1–3% antimony; antimony enhances electrolysis of water into hydrogen and oxygen during charging, leading to water loss. Therefore, in order to decrease the amount of water lost and for the production of hybrid and maintenance-free (MF) batteries, low-antimony–lead alloys (1.6–1.7 wt.% Sb) were used for grid production and many researchers have paid attention to the electrode characteristics of these alloys [2–4]. It has been shown in the literature that antimony in a lead–antimony electrode affects the microstructure and electrochemical behavior of active materials and corrosion layers on the electrode [5–11].

The use of low-antimony or antimony-free alloys is an effective way to minimize gassing and to achieve maintenance-free lead-acid batteries. Thus, new materials have been employed in grid manufacture, e.g., lead–calcium alloy. As little as 0.1% Ca in the lead alloy is sufficient to reduce gassing to a level where the battery can virtually be sealed and no water addition is required [12–13]. These alloys are significantly weaker than lead–antimony alloys. Lead–calcium alloys suffer higher rates of corrosion as the calcium content is increased, but higher calcium contents up to about 0.08 wt.% increase the mechanical properties of the alloys [1]. Tin additives to lead–calcium alloys improve its mechanical properties by changing the mode of precipitation from Pb₃Ca to the more stable Pb(Sn,Ca)₃ [14]. The use of lead–calcium alloys have lead to “passivation” phenomena at the positive plates; these are attributed to the formation of a poorly conducting oxide layer that has been identified as tetragonal lead oxide, referred as α -PbO. Alloying with tin (the original objective of which was to improve fluidity during casting) was found to be effective in decreasing grid passivation. Tin decreases the thickness of the PbO layer and increases the electronic conductivity of the passivation layer. The result showed that the conductivity increases sharply for alloying with a tin content higher than 1.5 wt.%. Also, alloying with tin increases the overvoltage of the oxygen and hydrogen evolution reaction [12].

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One of the major problems in the use of Pb–Ca–Sn alloys is the control of calcium content. Calcium is very susceptible to oxidation, which is especially severe when the alloy is agitated by stirring, pumping, or when it is accepting the return of trim strap from cast grids and rejects grids when the temperature at the melt pot is over 450 °C. A solution to the problems associated with calcium-fade is addition of minor amounts of aluminum (0.005–0.05%) to the lead–calcium alloy [13, 15].

In this report, the influence of lead alloy solidification temperature on the electrochemical behavior, especially on the overpotential for the evolution of hydrogen gas and on the electrode passivation in sulfuric acid solution within the range of 0.5–4.0 mol L⁻¹, was studied.

Experimental

The iron mold with cooling system and temperature control unit was used for preparing the working electrode. The working electrode was a wire with a geometric area of 0.5 cm². The composition of the alloys was Pb–Ca–Sn–Al (0.09%, Ca; 0.9%, Sn; 0.02%, Al) and Pb–Sb–Sn (1.7%, Sb; 0.24%, Sn). Sulfuric acid solution with various molar concentrations (0.5–4.0 mol L⁻¹) was used as electrolyte. The voltammograms of cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were obtained at a sweep rate 50 mV S⁻¹, in the potential range between hydrogen and oxygen evolution (–2.5 to +2.5), using a potentiogalvanostat of Behpajoo Co. Model BHP-2061-C. The experiments were carried out at room temperature (298 K) and the counter and reference electrodes were platinum black and Hg/Hg₂SO₄, respectively. Before the experiment, the electrode was mechanically polished with water-resistant emery paper and washed with acetone.

Micrographs of lead alloy electrodes were obtained with optical microscope and scanning electron microscope (SEM). The samples for the optical metallographic were buff-polished with Al₂O₃ powder and then chemically etched to clearly reveal grain boundaries and microstructures. The lead–antimony alloys were etched in 5% acetic acid solution [5] and the lead–calcium alloys with a 2:3 solution of glycerin in ethanol that contained small quantities of HNO₃ and H₂O₂ [16].

Results and discussion

The electrochemical behavior of lead alloys electrodes in sulfuric acid solutions are complex and depend on many variables, such as composition of alloys, sweep rate, kinds, and concentration of electrolytes. In this study, particular attention will be paid to the potential range and passivation behavior in various electrode with different solidification temperatures.

Electrochemical behavior of grids

Figure 1 shows voltammograms obtained at scan rate of 50 mV S⁻¹ for Pb–Ca–Sn–Al and Pb–Sb–Sn alloy electrodes that were prepared at the solidification temperature of 113 °C. According to the literature [5, 11], peaks (I), (II), and (III) are assigned to oxidation of Pb to PbSO₄/PbO and reduction of PbSO₄/PbO to Pb, respectively. The oxidation of tin takes place at the potential for the formation of PbSO₄/PbO [17]. Peak (IV) show the dissolution of Sb and its peak current was decreased rapidly after the second potential sweep. This suggests that the Sb atoms at the surface of the electrode almost have been dissolved during the first sweeping. Peak (V) relate to the reduction of PbO₂ to PbSO₄/PbO. The potential ranges in positive and negative direction were limited by the evolution of oxygen (B) and hydrogen gas (A). The peak current of calcium oxidation was not observed for the Pb–Ca–Sn–Al alloys, because its percentage in the alloy is very low.

Figure 2a–d shows the SEM of the lead–antimony and lead–calcium alloy electrodes prepared at different solidification temperatures after one cycle of charge and discharge in sulfuric acid solution.

The SEM pictures evidence that: (a) a greater amount of PbSO₄ is formed on the Pb–Ca–Sn–Al electrode surface than on the Pb–Sb–Sn electrode within one charge/discharge cycle. These observations agreed with the LSV voltammograms in Fig. 1, because, in this picture, the peak current of lead oxidation and reduction for lead–calcium electrode is higher than that for the lead–antimony alloy; (b) the crystals that formed on the Pb–Ca–Sn–Al electrode are larger in size than those on

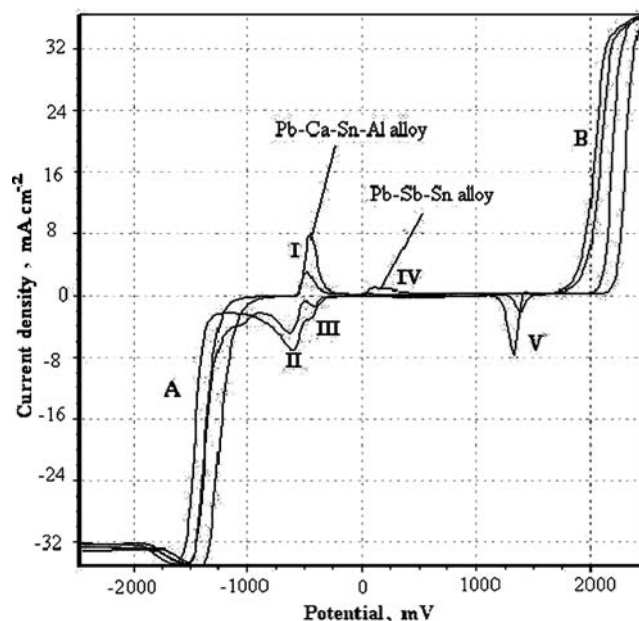


Fig. 1 Cyclic voltammograms of Pb–Ca–Sn–Al and Pb–Sb–Sn alloys at the scan rate of 50 mV S⁻¹; solidification temperature of 113 °C; H₂SO₄, 4 mol L⁻¹

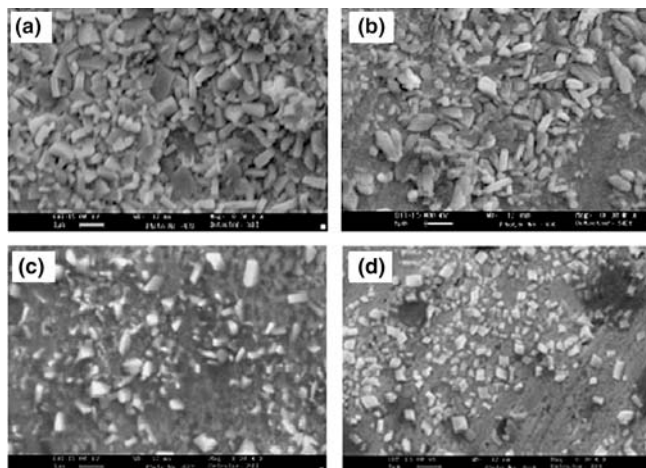


Fig. 2 The scanning electron micrographs (SEM) after using one cycle of charge and discharge for Pb–Ca–Sn–Al alloy at the solidification temperature of **a** 113 °C, **b** 157 °C and for Pb–Sb–Sn alloy at the solidification temperature of **c** 93 °C, **d** 131 °C

the Pb–Sb–Sn grid. This is due to the higher formation of PbSO_4 crystals in lead–calcium alloys and probably the formation of CaSO_4 , which may serve as a nucleation factor; (c) the distribution of PbSO_4 crystals is nonuniform, which indicates that they have formed in unevenly distributed active centers. The latter's concentration is lower in the Pb–Sb–Sn electrode; (d) a comparison between Fig. 2c, d indicates that the solidification temperature exerts a stronger influence on the processes in lead–antimony electrodes than in lead–calcium alloys.

On continuing with the cyclic voltammograms, the porosity and effective area of electrode surface gradually increases and the peak current of lead oxidation becomes higher.

Effects of solidification temperature on electrochemical behavior of lead alloys

The α -phase of lead–antimony alloy has hydrogen overvoltage being nearly the same as that of pure Pb. This alloy has a high overpotential for hydrogen evolution. But hydrogen overvoltage of the $\alpha+\beta$ form (eutectic alloy) is lower than the α alloy and has a higher catalytic activity. This overvoltage depends on the Sb content of the alloy and it decreases on increasing Sb concentration at the electrode surface.

Figure 3 shows the linear sweep voltammograms in the negative potential direction scanning for various Pb–Sb–Sn alloy electrodes prepared at different solidification temperatures, ranging from 93 °C to 163 °C. The potential ranges in positive and negative directions were limited by the evolution of hydrogen gas. Hydrogen overvoltage depends on the solidification temperature of the mold and each electrode has different electrochemical behavior for the evolution of hydrogen gas. The hydrogen overvoltage, in the first scan of linear sweep

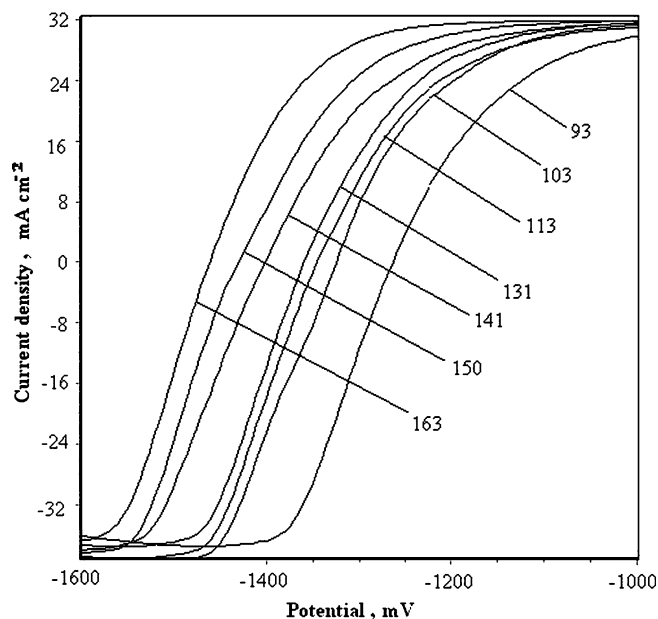


Fig. 3 The linear sweep voltammograms (LSV) of the Pb–Sb–Sn electrode in negative potential direction scanning for various electrodes produced in different solidification temperature; scan rate 50 mV S^{-1} ; H_2SO_4 , 4 mol L^{-1}

voltammograms, as a function of solidification temperatures at the current density of 16 mA cm^{-2} are shown in Fig. 4.

For Pb–Ca–Sn–Al alloys the behavior is different. According to Fig. 5, the overpotential for hydrogen evolution does not change for the electrodes prepared at various mold temperatures.

The above observations were confirmed by the optical microscopic structures of the electrode surfaces. Figure 6 shows the microscopic structures for the electrodes produced at different solidification temperatures. The grain structure of Pb–Sb–Sn alloy consists of a lead matrix surrounded by a network of second phase

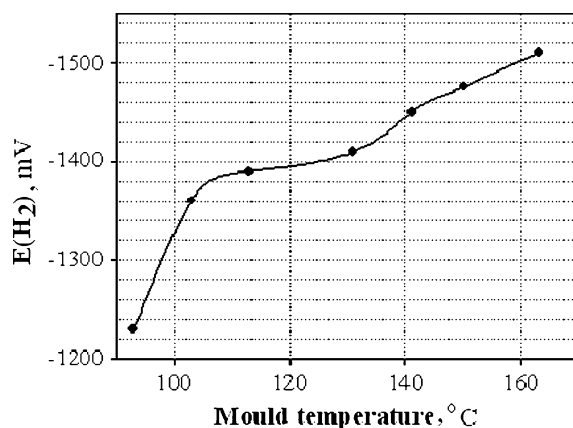


Fig. 4 Effect of solidification temperatures of Pb–Sb–Sn alloy on the hydrogen over voltage; current density of 16 mA cm^{-2} ; H_2SO_4 , 4 mol L^{-1}

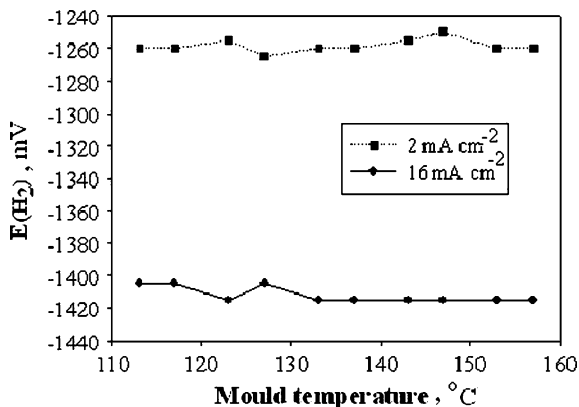


Fig. 5 Effect of solidification temperatures of Pb–Ca–Sn–Al alloy on the hydrogen over voltage; current density of 2 and 16 mA cm⁻²; H₂SO₄, 4 mol L⁻¹

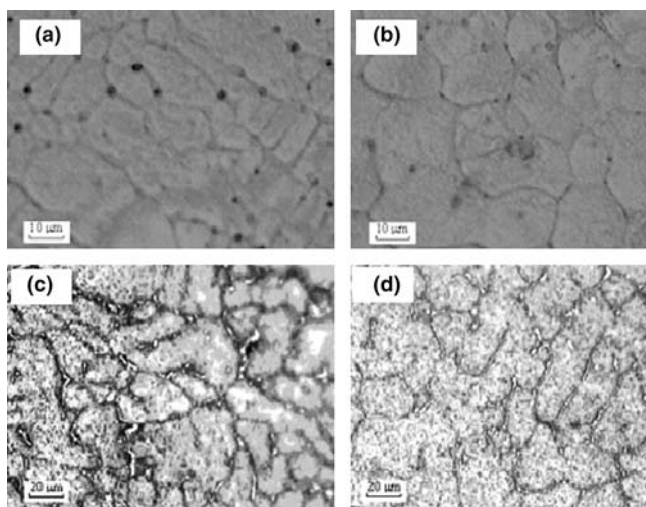
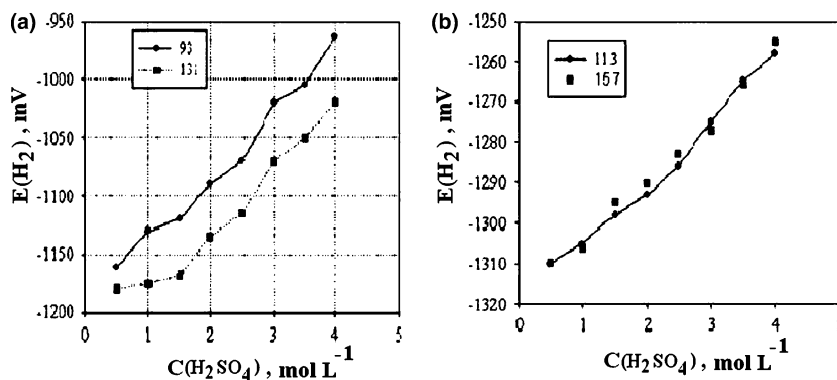


Fig. 6 The optical microscopic structures of the Pb–Ca–Sn–Al electrodes produced at the solidification temperature of **a** 113 °C, **b** 157 °C and Pb–Sb–Sn alloy at **c** 93 °C, **d** 113 °C

eutectic layers (β -phase, whose antimony content is high) depend on solidification temperature and for lead–calcium alloys, the black spots represent the calcium distribution or Pb(Sn,Ca)₃ phase.

Fig. 7 Effect of sulfuric acid concentration on the hydrogen overvoltage of **a** Pb–Sb–Sn alloy, **b** Pb–Ca–Sn–Al alloys at the mentioned solidification temperature; current density of 16 mA cm⁻²; H₂SO₄, 4 mol L⁻¹



The data in Figs. 3 and 4 indicate that for Pb–Sb–Sn grids the overvoltage of hydrogen increases with increase of the solidification temperature. Figure 6c, d shows that at a mold temperature of 93 °C, higher amounts of eutectic layers are formed between the α -Pb grains, thus the latter's surface hydrogen overvoltage is low. On increasing the temperature, the thickness of the eutectic layers on the electrode surface decrease, because when the molten materials (at the temperature of 430 °C) are injected into the mold (with lower temperature), at the first moment, the rate of heat transfer at the surface of mold is higher than middle melt, thus causing first α -Pb grains to form on the surface of electrodes, while in the interior the alloy is still molten. At a lower cooling rate of the lead alloy casting (for the higher mold temperature), impurities of lead alloys (e.g., antimony) penetrate to the molten bulk and decrease the amount of it that is present on the surface of the electrodes. At a higher cooling rate of the casting, the molten material solidifies very fast and the impurities do not have the opportunity to diffuse into the molten bulk and remain blocked at their positions. The reduced amount of eutectic on the grid surface leads to an increase in hydrogen overvoltage, which is actually observed in Figs. 3 and 4.

For Pb–Ca–Sn–Al alloys, the important factor that determines the overpotential of hydrogen evolution is the concentration of calcium, whose content in the alloy is very low; thus according to Fig. 6a, b the observed variation of calcium concentration on the electrode surface is very low and the hydrogen overvoltage is not dependent on the solidification temperature (Fig. 5).

The above phenomena are observed at various sulfuric acid concentrations (ranging from 0.5 mol L⁻¹ to 4.0 mol L⁻¹). Figure 7 shows this effect for Pb–Ca–Sn–Al and Pb–Sb–Sn alloys. The hydrogen overvoltage depends on the sulfuric acid concentration. On increasing sulfuric acid concentration, concentration of H⁺ ion is increased. Therefore, cathodic hydrogen evolution potential is shifted to more positive potentials.

In Fig. 8 a comparison of hydrogen overvoltage between lead alloys, pure lead, and pure tin is made. This pictures show that the hydrogen overpotential of Pb–Ca–Sn–Al alloys is higher than Pb–Sb–Sn alloys and pure lead (Pb–Sb–Sn alloy is prepared at a mold

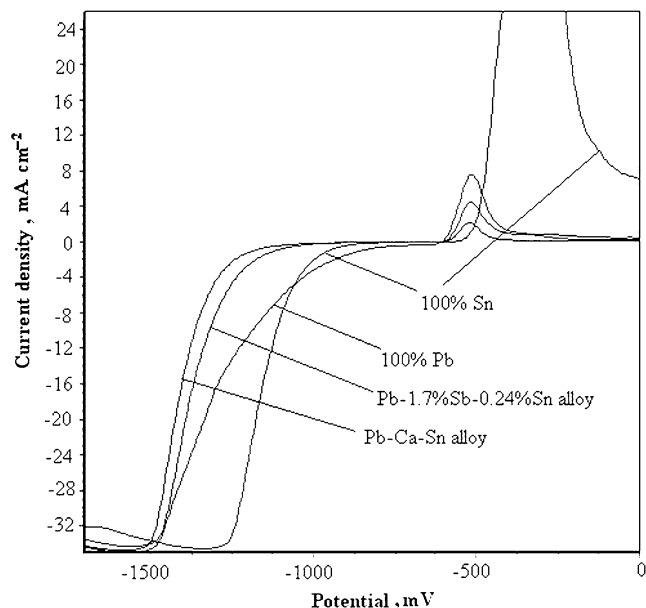


Fig. 8 The LSV of the various electrodes; scan rate 50 mV S^{-1} ; H_2SO_4 , 4 mol L^{-1}

temperature of $141 \text{ }^\circ\text{C}$). Also, hydrogen overvoltage in low and high current densities is reversed for pure lead and tin, which can be useful for prediction of tin behavior in lead alloys.

Conclusion

The electrochemical behavior of lead alloys has been studied as a function of the solidification temperature for preparation of the electrodes. The investigation was performed by means of CV, LSV, optical microscopy, and SEM.

The surface composition of electrodes depends on solidification temperature used for preparation of electrode. At a lower cooling rate of lead alloy casting (a higher mold temperature), impurities present in the lead alloys (e.g., antimony) penetrate to the interior of the mold and their concentrations decrease at the surface of the electrodes. Therefore, these electrodes show different

electrochemical behavior (mainly different overvoltage for hydrogen evolution). For Pb–Ca–Sn–Al alloys no change in hydrogen overvoltages were detected for different solidification temperatures. Also, in rapid cooling rates of casting, we observe greater passivation phenomena and remaining crystals after cycle of charge and discharge is higher.

Therefore, for the grid casting process, the control of the solidification temperature is very important in order to get a good electrochemical behavior for the grids. Also, in this case, the geometrical shape of the grid mold is affected due to the heat treatment behavior at the alloy casting, and this has an effect on the electrochemical behavior of grids.

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References

1. Prengaman RD (1997) *J Power Sources* 67:267
2. Danel V, Plichon V (1983) *Electrochim Acta* 28:785
3. Hammenoja E, Laitinen T, Sundholm G, Yli-Pentti A (1989) *Electrochim Acta* 34:233
4. Laihanen S, Laitinen T, Yli-Pentti A (1990) *Electrochim Acta* 35:229
5. Hirasawa T, Sasaki K, Taguchi M, Kanecho H (2000) *J Power Sources* 85:44
6. Manahov B, Pavlov D (1994) *J Electrochem Soc* 141:2316
7. Pavlov D (1993) *J Power Sources* 46:171
8. Ball RJ, Kurian R, Evans R, Stevens R (2002) *J Power Sources* 111:23
9. Hou-Tiana L, Jionga Y, Hai-Hea L, Ji-Huaaa Z, Wei-Fanga Z (2001) *J Power Sources* 93:230
10. Peterson I, Ahlberg E (2000) *J Power Sources* 91:143
11. Babic R, Melikos-Hukoric M, Lajqy N, Brinic S (1994) *J Power Sources* 52:17
12. Bui N, Mattesco P, Simon P, Steinmetz J, Rocca E (1997) *J Power Sources* 67:61
13. Hibbins SG, Timpano FA, Zuliani DJ (1996) US Patent No. 5,547,634
14. Prengaman RD (1995) *J Power Sources* 53:207
15. Zhong S, Liu HK, Dou SX, Skyllas-Kazacos M (1996) *J Power Sources* 59:123
16. Giess H (1995) *J Power Sources* 53:31
17. Petersson I, Ahlberg E (2000) *J Power Sources* 91:143