

Antimony-lead melts for high temperature electrochemical applications

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ABSTRACT

The electrochemical behaviour of an antimony-lead melt upon saturation with oxygen was studied to assess further prospects of such melts as potential anode materials for high-temperature fuel cells.

A perovskite ceramic was used as a robust current collector material. The related mechanisms of alloying and phase segregation were revealed at different melt oxidation levels using combined impedance spectroscopy and thermodynamic analysis.

1. INTRODUCTION

Liquid metals have emerged as exciting potential materials for fuel cell and battery applications due to their suitable redox potentials and active participation in electrode reactions [1–3]. Mixtures of antimony and lead may be especially promising for these applications due to relatively low melting temperatures and low cost, together with redox

potentials that are compatible with the oxidation potential of most forms of carbon and also suitable for potential batteries [4-6].

Figure 1 presents a possible application of liquid Sb-Pb melt for plastic waste utilization in electricity production [7].

2. EXPERIMENTAL DETAILS

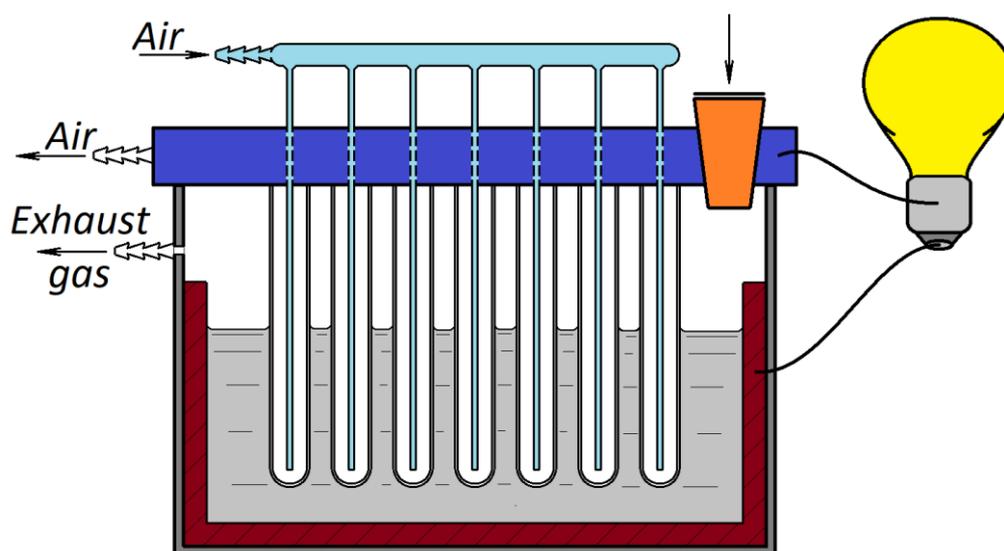


Figure 1. Principal scheme of plastic waste utilization reactor.

To investigate antimony-lead melts behavior in controlled conditions we made the following electrochemical cell. An yttria-stabilized zirconia tube was painted with platinum paste on the outer side to serve as an outer sensor electrode, allowing the oxygen activity in the melt to be determined. One YSZ disc covers the cell on the top and the other, used as oxygen pump, at the bottom.

Nevertheless, several problems were encountered with respect to the choice of current collector material. Platinum degrades in these conditions due to interreaction with the melt composition. Rhenium was also found to be unusable as it forms a volatile oxide at the working temperature of 700°C [8, 9].

To solve the problem, a perovskite ceramic disk of composition $(Y_{0.8}Ca_{0.2}Cr_{0.95}Ni_{0.05}O_{3\pm\delta})$ was, therefore, used [10]. This component is employed to function as both a current collector and as a potential probe for the melt. The corrosion stability of this ceramic was confirmed by long time tests of material in direct contact with antimony-lead melt at working temperature, followed by XRD analysis.

The entire volume of the YSZ cell was filled with previously mixed powders of antimony and lead (50/50% mol), corresponding to approximately 3.5 g of this mixture, with care taken due to prevent inhalation, due to the potential toxicity of the powder. The YSZ cell was then closed with top YSZ pellet and sealed with the help of a lower-temperature glass-ceramic sealant at 900 °C.

During the experiment oxygen was pumped inside the cell in portions equivalent to 200 Coulombs. After each step, the cell was completely disconnected from power supply and the sensor voltage was measured until its stabilization. This stable value was assumed to correspond to the attainment of equilibrium conditions between the melt and the oxygen amount introduced into the antimony-lead melt, as a function of the number of Coulombs passed.

The impedance spectra were recorded for each step, upon stabilization of the measured sensor potential in each case.

3. RESULTS AND DISCUSSION

Fig. 2 presents an example of the impedance response recorded for the antimony-lead melt, obtained at 700 °C at the oxidation degree of 97%. For clarity, the impedance corresponding to the offset on the real Z' axis (associated to the purely ohmic resistance) was subtracted. The impedance spectra show the existence of at least two semicircular responses in the measured frequency range.

The relaxation frequency of the low frequency term is shown to be strongly dependent on oxidation degree. This term reflects a diffusion process of oxygen exchange in the bulk volume of the melt. In contrast, relaxation frequency of the high frequency process is shown to be effectively independent of oxidation degree. This high frequency peak can be related to interfacial oxygen

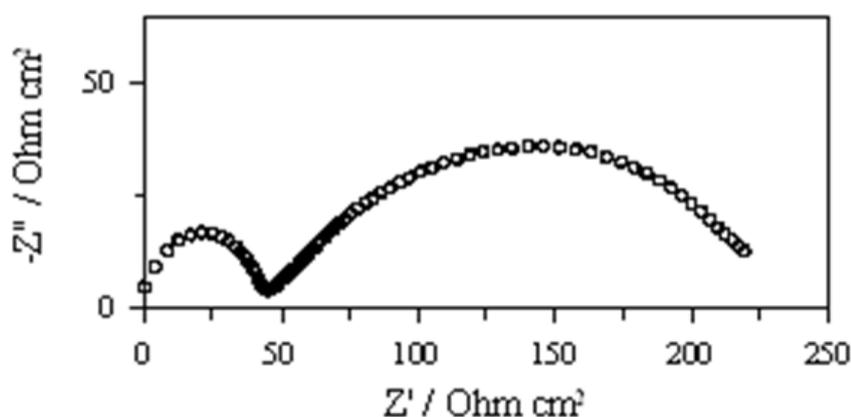


Figure 2. Impedance spectra of antimony-lead melt at 97 % oxidation degree.

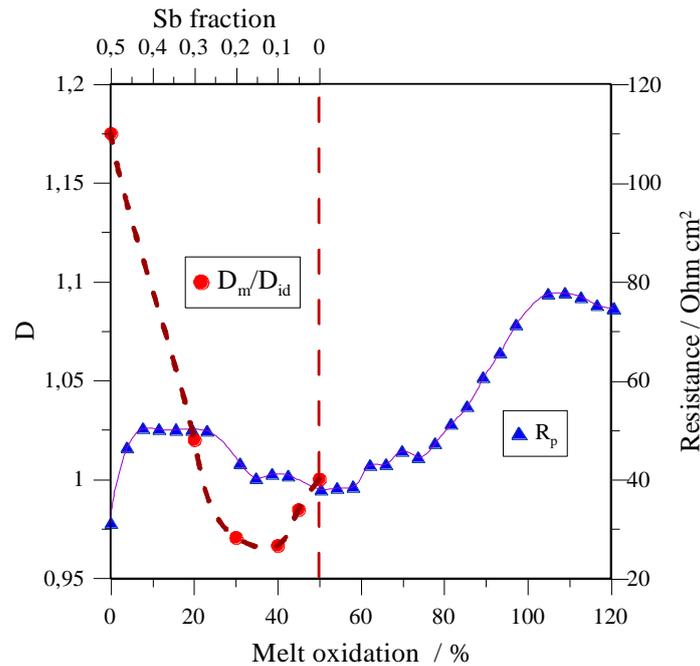


Figure 3. Polarization resistance values and degree of melt segregation

at various oxidation degrees. Horizontal line represents an ideal melt. The vertical line represents the total oxidation of Sb.

transfer from the zirconia pump to the metal mixture [11].

We have plotted impedance values vs oxidation degree in figure. 3. As antimony has a greater oxygen affinity than lead it can reduce any locally formed lead oxide to metallic lead. Therefore, during oxygen saturation, we firstly oxidize antimony metal from the mixture [12]. Therefore, we can replot this data as a function of the remaining antimony fraction in the melt.

Also, here we plot the degree of segregation of binary Sb-Pb alloy vs. antimony content, which as mentioned is also a function of oxidation degree (D_m/D_{id}). The degree of segregation reflects the level of reference to form melts with the same atoms as nearest neighbors and can be calculated from the available thermodynamic data [13, 14], where c_1 and c_2 are the concentrations of melt components, and $S_{cc}(0)$ is the long-wavelength limit of the concentration-concentration fluctuation:

$$D = \frac{c_1 c_2}{S_{cc}(0)} \quad (1)$$

A ratio greater than unity represents a compound forming liquid alloy formation, whereas values lower than unity reflect a segregated melt.

Upon oxidation, in the first stage of a compound forming melt, all characteristics shows almost constant behaviour as antimony metal is oxidised from a well distributed melt composition.

Later, as more antimony metal is oxidized, the melt composition passes into the segregation zone where lead and antimony separate in the melt composition. At this point, the lead falls to the bottom of the melt due to its higher density and is in contact with the pump surface. For this reason, the high frequency resistance, corresponding to interfacial transfer of oxygen from the pump surface to the melt, is shown to change. Moreover, at the bottom of the melt no antimony metal is now available to reduce the lead oxide and, hence, the lead oxide must diffuse upwards to meet the remaining antimony metal and be reduced. Consequently, the low frequency resistance also increases from this point, with an even greater increase shown once all antimony is oxidized, as observable by the variations in the total polarization resistance R_p in figure 3.

4. CONCLUSIONS

In conclusion, the current work forms a robust test equipment and technique for investigations of the

electrochemical behaviour of melts, which can allow the detailed study of different compositions of metal melt electrodes and their application in electrochemical devices. The development of such a method was shown be critical due to the very aggressive environments present in this type of experiment.

The presented experiments also show the perspectives of using antimony-lead melt electrode for high temperature electrochemical cells and the importance of assessment of melt segregation on resultant electrochemical properties.

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