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Galvanostatic charge–discharge tests, ^{57}Fe and ^{119}Sn Mössbauer and XRD measurements on novel Sn-Ni-Fe electrodeposits

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Abstract Novel Sn–Ni–Fe ternary alloys were successfully deposited by pulse plating technique from an electrolyte based on sodium gluconate which acts as a complexing agent. XRD results revealed the predominantly amorphous character for the majority of the deposits. ^{57}Fe and ^{119}Sn conversion electron Mössbauer spectroscopy indicated the formation of a paramagnetic amorphous alloy using a short on-pulse duration and where the Fe content was less than 22 wt.%. Galvanostatic charge–discharge tests of the novel Sn-Ni-Fe deposits were carried out in a model Li-ion cell and indicated that the Sn-Ni-Fe alloys have potential as an electrode material.

Keywords Sn-Ni-Fe electrodeposit · Pulse plating · Amorphous coating · ^{57}Fe and ^{119}Sn Mössbauer spectroscopy · X-ray diffractometry · Galvanostatic tests · Batteries

1 Introduction

Tin–nickel–iron (Sn–Ni–Fe) ternary alloys have significant potential for technological developments not only in soft magnetism and for environmentally acceptable corrosion resistant materials but also in producing high performance electrodes for Li-ion batteries. Earlier works [1, 2] showed that novel Sn–Ni–Fe ternary alloys could be successfully obtained by direct current (DC) electrochemical deposition.

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Table 1 Deposition parameters, composition and thickness of the pulse plated Sn-Ni-Fe coatings

No	Parameters	Sn wt.%	Ni wt.%	Fe wt.%	Thickness (μm)
1	$t_{on} = 0.01$ s $t_{off} = 0.49$ s -100 mA/cm^2, 900 s	60.21	2.36	37.43	0.8
2	$t_{on} = 0.01$ s $t_{off} = 0.19$ s -100 mA/cm^2, 900 s	82.43	3.14	14.42	1.2
3	$t_{on} = 0.1$ s $t_{off} = 0.9$ s -100 mA/cm^2, 300 s	63.08	7.02	29.90	n.a.
4	$t_{on} = 0.01$ s $t_{off} = 0.49$ s -100 mA/cm^2, 600 s	71.02	8.39	20.59	0.97
5	$t_{on} = 0.01$ s $t_{off} = 0.49$ s -200 mA/cm^2, 600 s	67.84	9.03	23.13	0.55
6	$t_{on} = 0.01$ s $t_{off} = 0.49$ s -300 mA/cm^2, 600 s	67.56	13.37	19.07	0.55
7	$t_{on} = 0.01$ s $t_{off} = 0.49$ s -400 mA/cm^2, 600 s	72.27	12.41	15.32	0.14

^{57}Fe and ^{119}Sn conversion electron Mössbauer spectroscopy (CEMS) and powder X-ray diffractometry (PXRD) investigations showed that these ternary alloys were essentially amorphous and ferromagnetic.

A pure tin anode has a high specific theoretical capacity (990 mAh/g) but poor cyclic ability compared to the more generally used graphite anodes [3]. Sn-Ni-Fe amorphous alloys have the potential to give relatively high capacity with good cyclic ability for future Li-ion battery applications.

The aim of these studies was to produce novel tin-based Sn-Ni-Fe alloy coating structures for electrode materials using environmentally and economically acceptable processes. For these investigations ^{57}Fe Mössbauer spectroscopy, X-ray diffractometry, SEM EDAX analysis and galvanostatic charge–discharge tests were carried out.

2 Experimental

A Sn-Ni-Fe electrolyte was set up with a pH of 6.00 using an aqueous solution containing 0.3 M NaCl, 0.3 M H_3BO_3, 0.02 M $SnSO_4$, 0.05 M $NiSO_4$, 0.02 M $FeSO_4$, 0.2 M Sodium gluconate with small addition of antioxidant and surfactant. The electrodeposition was carried out in a glass cylindrical cell at 20 °C with agitation and using different pulsed current parameters which are listed in Table 1. The anode used was high density carbon and was placed at 1 cm distance from the cathode. The samples were electrodeposited on the one side of a 25 μm copper foil, which was treated in 66 wt.% phosphoric acid solution, at a constant current of 1 A cm^{-2} for 2 min and thereafter rinsed in pure water prior to electrodeposition.

Powder X-ray diffractograms of the samples were measured by a computer controlled DRON-2 X-ray diffractometer using $\mathrm{Fe}_{K\alpha}$ radiation and a β filter. The diffractograms were recorded between 5° and 95° in 2θ, with a goniometer scanning speed of 0.2° min^{-1} at room temperature. The evaluation of the XRD patterns was made by the EXRAY code. For identification of the phases the ASTM X-ray diffraction data were used.

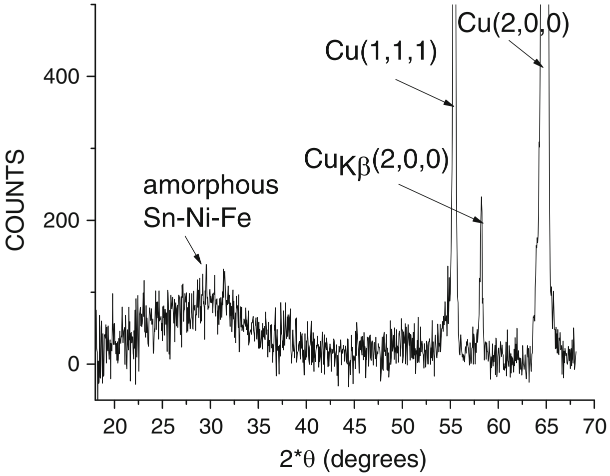

Fig. 1 XRD of pulse plated Sn-Ni-Fe sample 1

^{57}Fe and ^{119}Sn conversion electron Mössbauer spectra of electrodeposited samples were recorded using a conventional Mössbauer spectrometer (WISSEL) working in constant acceleration mode. The γ-rays were provided by a 3×10^9 Bq ^{57}Co/Rh and by a 5×10^8 Bq Ca^{119m}SnO$_3$ sources. The measurements were performed at room temperature. The Mössbauer spectra were analyzed by least-square fitting of Lorentzian lines by the help of the MOSSWINN code [4].

A model Li-ion cell was used for testing the electrochemical performance. Lithium metal foils were used as the reference and counter electrodes. There was no separator in the cell. The electrolyte was 1 M LiClO$_4$ dissolved in EC + DEC (1:1 by volume) solution. The cells were assembled in a glove box filled and purged with argon gas (less than 10 ppm of water). Cells were cycled at room temperature between 0.02 V and 2 V versus Li/Li$^+$ at a constant current of 0.2 C calculated from the tin content.

3 Results and discussion

A typical XRD (Fig. 1) for the pulse plated Sn-Ni-Fe samples (Table 1) indicates the predominantly amorphous character for the majority of the deposits. Due to the small thickness of the deposit, the copper substrate reflections can be also indentified in the XRD since the penetration depth of the X-ray is much higher than the thickness of the deposit.

Figure 2 shows ^{57}Fe and ^{119}Sn Mössbauer spectra for the pulse plated deposits prepared at two significantly different on/off periods of pulses. The ^{57}Fe and ^{119}Sn spectra of the Sn-Ni-Fe deposit (sample 3, Table 1) which was plated at $t_{on} = 0.1$ s shows a magnetically split spectra with broad lines with average hyperfine field of 21.6 T and 1.2 T for ^{57}Fe and ^{119}Sn, respectively, indicating a predominantly ferromagnetic amorphous Sn-Ni-Fe alloy, similar to the results reported for DC electrodeposition [1, 2]. However, for the samples (typically sample 4, Table 1) plated using $t_{on} = 0.01$ s, the ^{57}Fe and ^{119}Sn spectra exhibit only paramagnetic components with an average quadrupole splitting of 0.38 mm/s and 1.23 mm/s for ^{57}Fe and ^{119}Sn, respectively. These latter spectra are associated with a paramagnetic amorphous

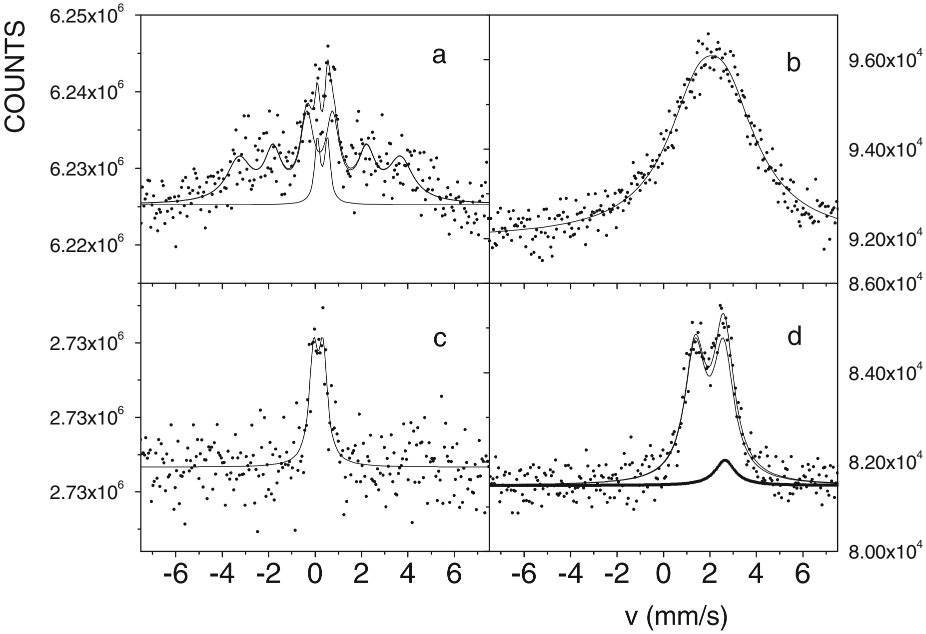

Fig. 2 RT ^{57}Fe (**a** and **c**) and ^{119}Sn (**b** and **d**) Mössbauer spectra of novel Sn-Ni-Fe deposits pulse plated at $t_{on} = 0.1$ s $t_{off} = 0.9$ s (**a** and **b**) and $t_{on} = 0.01$ s $t_{off} = 0.49$ s (**c** and **d**)

structure where the XRD reveals the amorphous character of the samples. Thus the pulse plating with the much shorter on-pulse ($t_{on} = 0.01$ s) alternatively provides a paramagnetic amorphous phase. The occurrence of amorphous phase in paramagnetic state can be effectively explained by the compositional changes occurring between the coatings plated with the short and long pulse time depositions. It was noted that Fe content is significantly higher (29.90 wt.%) while the Sn (63.08 wt.%) content is significantly lower in the sample 3 plated at $t_{on} = 0.1$ s compared to those deposited at $t_{on} = 0.01$ s (sample 4, Table 1) where all other plating conditions were the same. Thus paramagnetic amorphous alloy phases are found where the iron content of coating is below 22 wt.% which means no ferromagnetic coupling appears in these alloys thus emphasizing the paramagnetic character of the alloys.

It can be seen from Table 1 for the samples deposited using $t_{on} = 0.01$ s and $t_{off} = 0.49$ s that increasing current density causes the Fe content to decrease, the Ni content to increase, while the Sn content remains relatively the same.

It is believed that finer particle size distribution could be deposited using the short pulse time deposition ($t_{on} = 0.01$ s) compared to the long pulse time deposition ($t_{on} = 0.1$ s). Where $t_{on} = 0.01$ s the much shorter pulse deposition time could lead to re-nucleation of the alloy growth with each pulse cycle thus generating a large number of growth centres and hence a much finer particle size distribution. This difference is not surprising as conditions at the catholyte-electrode interface could be expected to be significantly different with a tenfold difference in the on-pulse time. Hydrogen reduction could also have an effect on the growth morphology where it is possible that the much shorter pulse on time could considerably inhibit

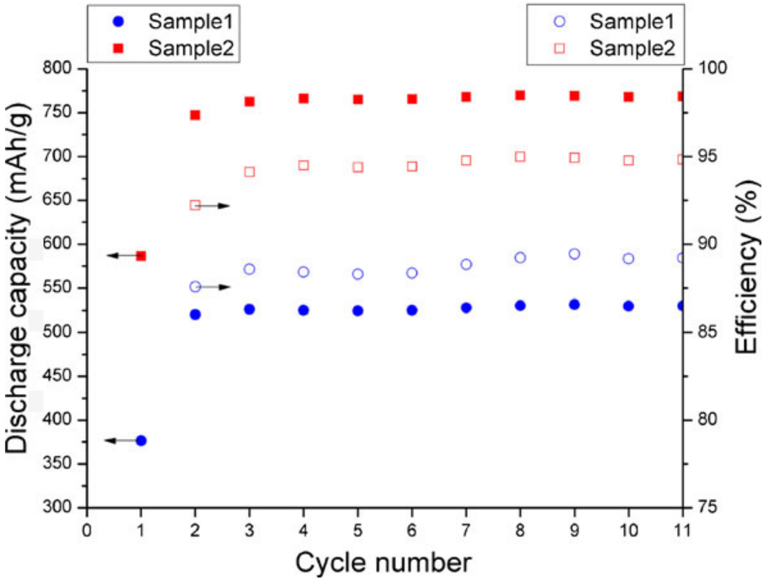

Fig. 3 Galvanostatic charge–discharge tests of Sn-Ni-Fe deposits

hydrogen formation thus facilitating more nucleation sites at the cathode. The finer particle size distribution generated using $t_{on} = 0.1$ s would as a consequence have a much greater surface area per unit volume which would be an attractive morphology for an electrode to be used in Li-ion batteries. However, the results of the SEM measurements are not sufficiently convincing, therefore further detailed SEM studies are needed to validate this hypothesis and will be the subject of further research.

The galvanostatic charge-discharge test results on selected samples are shown in Fig. 3. The best capacity value after 1 cycle, 755 mAh/g, was achieved for sample 2, when the charging efficiency was 95 %. The discharge capacity remains constant after 10 cycles and reaches the 80 % Depth of Discharge (DOD) after 345 cycles, which was calculated from a fitted trend line. Compared with carbon anodes, which have a specific discharge capacity of 320 mAh/g, the pulse plated Sn-Ni-Fe system exhibiting the paramagnetic amorphous structure gives a 2.35 times higher specific capacity with a sustainable cycle life.

4 Conclusion

A range of novel paramagnetic and ferromagnetic amorphous Sn-Ni-Fe alloys can be successfully electrodeposited using a pulse plating system where $t_{on} = 0.01$ s and t_{off} varies between 0.19 s and 0.49 s. It is considered from the theory on nucleation and growth of alloys that it is likely that the paramagnetic amorphous alloys obtained at $t_{on} = 0.01$ s and $t_{off} = 0.49$ s have a much finer structure.

^{57}Fe and ^{119}Sn conversion electron Mössbauer spectroscopy revealed that these novel alloys occur in form of paramagnetic phase using pulse plating where $t_{on} = 0.01$ s and $t_{off} = 0.49$ s and where the Fe content is below 22 wt.%.

The galvanostatic charge–discharge tests indicated that Sn-Ni-Fe alloys obtained show potential as a new anode material for Li-ion battery.

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