

ELECTROCHEMICAL IMPEDANCE AND Co CONTENT EFFECT OF LaNi₅-BASED INGOT ELECTRODES

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Abstract. AB₅ type alloys of composition LaNi_{4.3-x}Co_xMn_{0.4}Al_{0.3} ($x = 0, 0.25, 0.5, 0.75, 1.0$) are prepared and carefully annealed to make ingot electrodes which allow to measure the impedance on its well defined flat surface. The impedance data were analysed according to an equivalent circuit to find kinetic parameter as charges transfer resistance R_{ct} . Variation of real part Z_r has been examined. All these analyses have been carried out considering the influence of Co ratios x . It is found that the suitable Co ratio is statistically $x = 0.75$.

Keywords: Ni-MH, LaNi₅ materials, ingot electrode, impedance, EIS, Co substitution.

INTRODUCTION

In the recent years, metal hydride batteries have become increasingly popular as an alternative to Ni-Cd. In addition to the environmental benefits, they also have high discharge rates, long cycling stability and high energy-storage capacity (30—50% higher than Ni-Cd batteries) [1, 2]. The electrochemically active materials used in these batteries are LaNi₅ based. In order to obtain the optimum performance, partial substitutions of the alloy composition with transition metals and rare earth metals have been investigated. Sakai et al [3] have studied AB₅ alloys with different elements substitution, as Mn, Cr, Al, Co and Cu. It was found that the cycle-life improves upon the substitution of Ni with the ternary solute in order Mn < Ni < Cu < Cr < Al < Co.

Co is a thermodynamically and kinetically important substituting element [4, 5]. However, the mechanism and the kinetics of the electrochemical behaviours of Co substitute have been still not clear [6]. That makes a subject of many recent researches [4—10]. Fundamental knowledge of positive action of Co additive in batteries negative electrodes materials is necessary to find other substituting elements, which are lower cost and more effective.

Beside that, many experimental techniques have been developed to study the behaviour of these materials [11—14], especially the electrochemical impedance measurement [5, 7, 12—20].

Electrochemical impedance spectroscopy (EIS) is an essential tool to study a mechanisms of electro-

chemical process, in particular the electrochemical charge-discharge process of Ni-MH batteries. EIS technique allows studying the electrochemical reaction kinetics and particularly some reaction steps.

Impedance analyse of metal hydride electrodes is an established characterisation technique, considered as a non-destructive [12]. Following an impedance measurement, it is usually to research an equivalent circuit or to do a mathematic simulation.

In this paper, ingot electrodes of the LaNi_{4.3-x}Co_xMn_{0.4}Al_{0.3} alloys, where x is largely varied in range of 0 to 1, have been prepared and utilised to study kinetic and mechanistic phenomena using EIS technique. The Co content effect on the electrodes behaviours has been also examined throughout impedance analysis.

EXPERIMENTAL PROCEDURE

Negative electrode materials of composition LaNi_{4.3-x}Co_xMn_{0.4}Al_{0.3}, $x = 0, 0.25, 0.5, 0.75$ and 1.0, has been chosen. The preparation of the materials comprise of many steps (figure 1). The raw metallic materials are of high purify. The most significant step is annealing at 1100° C during 7 days. All preparation were carried out at ITIMS and ITT (VAST).

Figure 2 presents the XRD patterns of the prepared materials with different Co ratios x . The crystalline structure of the materials are hexagonal as that of CuCa₅, and all samples of different Co ratios possess this structure.

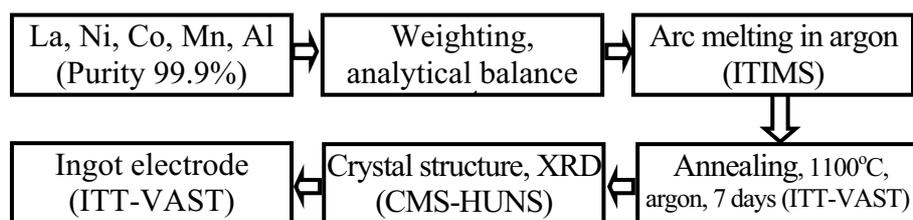


Fig. 1. Block diagram of samples preparation steps.

The sample ingot electrodes were formed, with diameters 0.2—1 cm, thickness 0.1—0.5 cm. The electrodes are contacted and covered securely by epoxy resin. The ingot electrodes surface was subsequently polished using abrasive paper grade 600, 800 and 1000. It was then several times cleaned, washed, dried, and examined using SEM Jeol 5410LV system.

Electrochemical cell is a three electrodes system: working electrode (WE), referent electrode (RE, saturated calomel electrode (SCE)), and counter platinum mesh electrode (CE). The referent electrode is connected with electrolyte by KCl-bridge and intermediate vessel containing KOH 6M solution, and second KOH-bridge. All of electrochemical impedance measurements are carried out using AUTOLAB PGSTAT 30 system with FRA (Frequency Response Analyzer) 4.7 software, at 100 kHz to 10 mHz and amplitude 5 mV. To control measurement process, a PC with special software is used, also for collecting and analysing experimental data.

RESULT AND DISCUSSION

The typical Nyquist plots of the electrochemical impedances of the ingot electrodes are presented in figure 3. As can be seen, the impedances have only one semicircle, exception of the first one with $x = 0$ at $E = -0.9V$, where two final points are typical of a diffusion impedance. However, the diffusion impedance

is not significant at the applied frequencies range [12, 13] with ingot electrodes.

The simplified equivalent circuit of those impedances composes two principal components in parallel: capacitance of double layer C_{dl} and charge transfer resistance R_{ct} . The diffusion impedance can be represented by a component W in series with R_{ct} , as shown in figure 4. It is possible to fit the experimental data finding R_{ct} and C_{dl} , two parameters related to kinetics of electrochemical reaction. Variation of these parameters with polarisation potentials at different Co ratio x is presented in figure 5.

In general, R_{ct} increases with increasing applied potentials, however, C_{dl} decreases, with exception C_{dl} of sample M4 at Co ratio $x = 0.75$. R_{ct} is an important kinetic parameter [12]. In the studied electrochemical system, there is only hydrogenation / des-hydrogenation charge transfer reaction which is significant, so that from R_{ct} data one can estimate the charge transfer current using simplified equation $J_{ct} = RT/FR_{ct}$ [21]. It is evident that the smaller is R_{ct} , the more important is J_{ct} . For sample M2 $x = 0.25$, at $E = -0.9V$ the R_{ct} value attains a maximum, that means the rate of charge transfer J_{ct} is minimal.

For the other applied potentials, the values of R_{ct} are nearly the same. In order to find the Co ratio x suitable for the reaction, R_{ct} variation according to x was examined (figure 6).

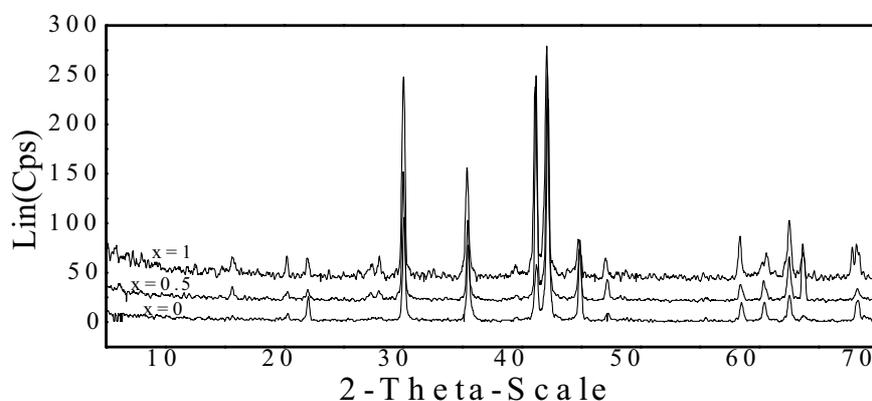


Fig. 2. XRD patterns of $\text{LaNi}_{4.3-x}\text{Co}_x\text{Mn}_{0.4}\text{Al}_{0.3}$, $x = 0$, $x = 0.5$ and $x = 1$.

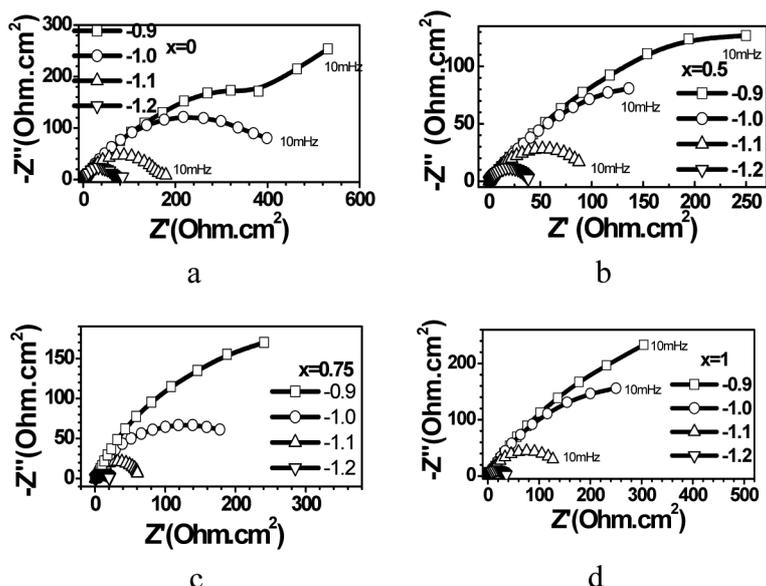


Fig. 3. Typical Nyquist plots of impedance of ingot electrodes, Co ratio $x = 0$ (a), 0.5 (b), 0.75 (c) and 1.0 (d), at different polarization potentials.

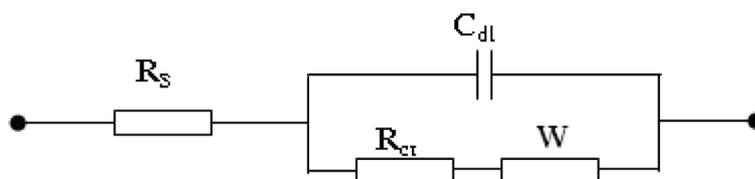


Fig. 4. Equivalent circuit for the impedance of the ingot electrodes, R_s : solution resistance, R_{ct} : charges transfer resistance, C_{dl} : double layer capacitance, W : diffusion impedance.

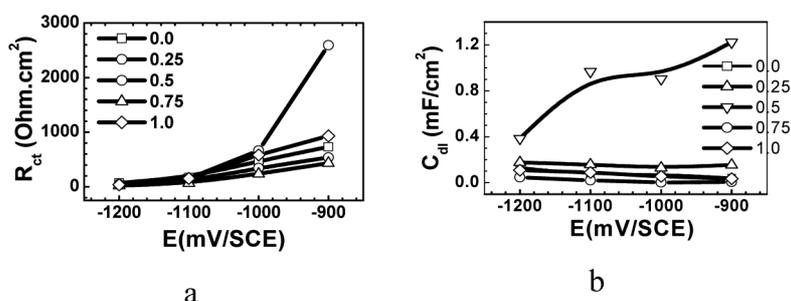


Fig. 5. Variation of R_{ct} (a) and C_{dl} (b) as a function of polarisation potential E , the inserted numbers are Co ratio x .

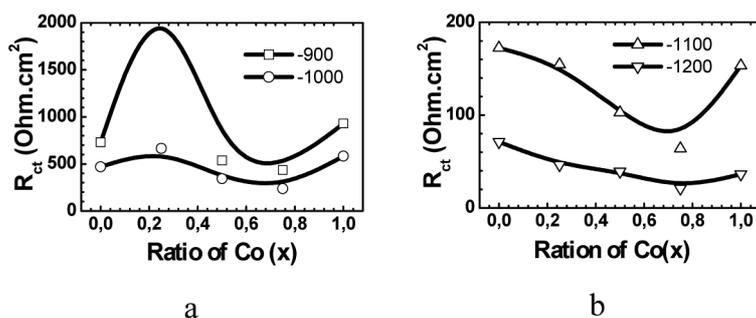


Fig. 6. Dependency of R_{ct} on the Co ratio x at -0.9 V, -1.0 V (a) and at -1.1 V, -1.2 V (b).

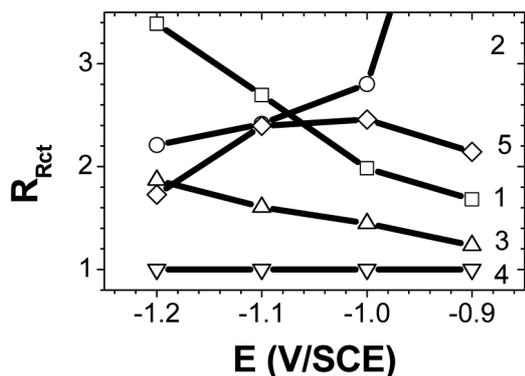


Fig. 7. Variation of R_{ct} ratio $R_{Rct} = R_{ctM1}/R_{ctM4}$, on polarisation potential E . 1 — R_{ctM1}/R_{ctM4} ; 2 — R_{ctM2}/R_{ctM4} ; 3 — R_{ctM3}/R_{ctM4} ; 4 — $R_{ctM4}/R_{ctM4} = 1$; 5 — R_{ctM5}/R_{ctM4} .

It is evident that for $x = 0.75$, R_{ct} are minimal at the all applied potentials, corresponding to the maximum rate of the hydrogen charge transfer reaction. This suitable Co ratio $x = 0.75$ has been also reported previously [22—26]. However, the value $x = 0.5$ gives R_{ct} very close to that at $x = 0.75$. The ratio $R_{Rct} = R_{ctM3}/R_{ctM4}$ is nearly 1, especially at $E = -0.9$ (figure 7). That means that at range $x = 0.5—0.75$ there is approximately the same kinetics of charge-discharge process.

Impedance divides usually to real part Z_r and imaginary part Z_i . Z_r characterises the real resistance proportion contributing to the total impedance at given frequency. For the LaNi_5 based ingot electrodes, Z_r represents the possibility to transfer the charges of hydrogen redox throughout the interface at given frequency. For the lowest frequencies, Z_r approaches the intrinsically kinetic parameter R_p or R_{ct} . Figure 8 presents a variation of Z_r as a function of frequencies in log scale.

It is evident that at high frequencies, Z_r values are small and closing each other. For the rest, Z_r evidently depends on Co ratios. For $x = 0.5$ and 0.75 , Z_r are very approximate and together achieve minima for all frequencies range. However, at $E = -1.2\text{V}$, both Z_r are always the smallest in comparison with those at the other Co ratios. Between Z_r at $x = 0.5$ and 0.75 , there is an alternative exchange of minimal values according to frequencies range. There is a compromising of two Co ratios effect at 0.5 and 0.75 .

It is reasonable to consider an existence of fast and slow 'charges', transfer of which can be considered as fast (capable response to high frequencies), and slow (the response only manifests at low frequencies), respectively. At the lowest frequencies, the all fast and slow charges are similarly affected by the impedance signals and their responses to these lowest frequencies

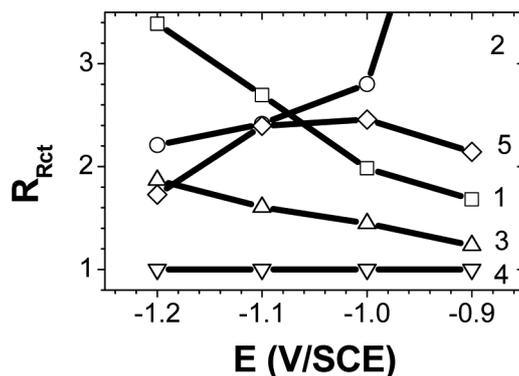


Fig. 8. Variation of real part of the electrodes impedance Z_r at $E = -0.9\text{ V}$ (a), and at $E = -1.2\text{ V}$ (b), inserted numbers are Co ratios x .

signals are together joined and undistinguishable. This is interesting to correlate the high rate discharge possibility of the Ni-MH batteries with fast responses of hydrogen redox, with considering frequencies range.

For the all Co ratios studied in this paper, the value $x = 0.75$ nevertheless is statistically the most suitable for the electrochemical hydrogenation / des-hydrogenation on the ingot electrode, corresponding to the previous results of space charges studies [22, 23], and others [24—26]. At $x = 0.75$ the space charges quantity at interne side of the interface solid/liquid achieves minimal values, in comparison to the other Co ratios [22, 23], corresponding to the highest rate of hydrogen redox, and here equivalent to the lowest R_{ct} .

CONCLUSION

Electrochemical behaviours of $\text{LaNi}_{4.3-x}\text{Co}_x\text{Mn}_{0.4}\text{Al}_{0.3}$ alloys in KOH 6M have been studied on ingot electrodes which possesses an indisputable advantage in elimination of the surface geometry effect.

Electrochemical impedance spectroscopy is helpfully practical tool enable to evaluate kinetic and mechanistic parameters, of which the charges transfer resistance R_{ct} is one of the most important kinetic representant. At Co ratio $x = 0.75$, the obtained resistance R_{ct} attains minimum meaning the maximum of hydrogen redox rate.

According to the variation of Z_r , one can correlate frequencies effects on Z_r with a response rate of the ingot electrodes reaction to the impedance signals. There are fast responses corresponding to high frequencies, and a slow response appeared only at low frequencies. At the lowest frequencies, both the fast and the slow responses join together becoming undistinguishable. The frequencies effect seemly concerns

also the effects of applied polarisation and Co contents, which do not seem too simple as it has been considered.

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