

NEW ASPECT OF ELECTROCHEMICAL IMPEDANCE ANALYSE CONCERNING Co EFFECT ON LaNi_5 BASED INGOT ELECTRODES

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Abstract. AB_5 type alloys of composition $\text{LaNi}_{4.3-x}\text{Co}_x\text{Mn}_{0.4}\text{Al}_{0.3}$ ($x = 0, 0.25, 0.5, 0.75$ and 1.0) are prepared and annealed to make ingot electrodes which allow to measure the impedance on its well defined flat surface. From experimental data of the impedance, the real part Z_r and the capacitance C have been examined according to the applied corresponding frequencies and polarisation potentials. It is found that Z_r , and hence suitable Co ratios x , are affected in the same time by applied potentials and impedance signal frequencies. There are two suitable Co ratios $x = 0.5$ and $x = 0.75$ corresponding to two opposite processes, one of charging at $R = -1.2\text{V}$ and the other of discharging at -0.9V , respectively. It was found that there are transitional frequencies and potentials for the passage of the first suitable Co ratio to the second.

Keywords: LaNi_5 materials, ingot electrode, impedance, EIS, Co contents, transition.

INTRODUCTION

In Ni-MH batteries based on AB_5 type negative electrodes, Co is a thermodynamically and kinetically important substituting element [1, 2]. Fundamental knowledge of Co effect on batteries negative electrodes behaviours is necessary to research other substituting elements, which are with lower costs than Co. However, the mechanism of Co additives effect on electrochemical properties of LaNi_5 type materials has been not clearly understood [3]. Many recent researches have dealt with this question, almost basing on the electrochemical kinetics of hydrogen redox on LaNi_5 type electrodes [1—11].

Electrochemical impedance spectroscopy EIS is the most useful tool for the mechanistic investigation on the electrochemical charge-discharge process of Ni-MH batteries [2, 6, 12—21]. That is enabling to evaluate the charges transfer resistance R_{ct} , one of the most important kinetic parameters [12]. Using EIS technique, the Co contents effect has been studied. It was found that at $x = 0.75$ the space charges quantity at internal side of the interface solid/liquid decreases to minimum [22, 23], corresponding to a high reaction rate of hydrogen redox, and to a low R_{ct} . The Co ratio $x = 0.75$ seems optimal that decreases R_{ct} , increases the stability of charge-discharge process and prolongs the cyclic lifetime of the electrodes [24, 25].

The electrochemical kinetic and mechanistic researches using EIS technique have been carried out almost on the electrodes prepared from powder materials. That is unable to define electrodes surfaces geometry, exclusive of second effect of additives given in electrodes prepared from powder materials. An analysis of hydride electrodes impedance is an established technique [12], and has been exclusively developed with proposed equivalent circuits and mathematic simulations. These analysis techniques take into account certain entire range of applied frequencies hence the obtained results possess statistic characters. Par example, an equivalent circuit is usually valuable in certain range of frequencies, and two determined parameters R_{ct} and C_{dl} get a statistic character accumulated from all frequencies taken in analysis.

Impedance Z of a system 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 frequencies, and Z_i can be used for the capacitance C calculation, also at given frequencies. For the LaNi_5 based ingot electrodes, at given frequencies, the real part Z_r represents the possibility to transfer the charges throughout the interface of redox reaction of hydrogen, the capacitance characterises in general the charges quantity capable to pass the interface — capacitor such as a double layer [27]. For the

lowest frequencies, Z_r approaches the intrinsically kinetic parameter R_{ct} (or R_p some times), and calculated C approaches a pseudo-capacitance with very high, according to the characteristics of electrochemical impedance.

The LaNi_5 ingot electrodes are helpful for the fundamental research on the electrochemical behaviours of the LaNi_5 based materials [21, 27, 28]. Especially the thickness of the surface-active layer has been for the first time discussed basing on the experimental data and the determined surface capacity Q_s values. The EIS studies on ingot electrodes have revealed the most suitable value $x = 0.75$ for the electrochemical hydrogenation / des-hydrogenation.

In order to understand better electrochemical behaviours of the materials with variable Co contents, in this paper we will analyse the impedance data of ingot electrodes of $\text{LaNi}_{4.3-x}\text{Co}_x\text{Mn}_{0.4}\text{Al}_{0.3}$ materials ($x = 0, 0.25, 0.50, 0.75$ and 1.0), with considering the frequencies effect together with that of polarisation.

EXPERIMENTAL PROCEDURES

The $\text{LaNi}_{4.3-x}\text{Co}_x\text{Mn}_{0.4}\text{Al}_{0.3}$ materials were prepared using arc melting technique. After annealing at 1100°C during 7 days, the obtained materials was analysed to find out its chemical composition and crystalline structure. The prepared materials have stoichiometric chemical composition as $\text{LaNi}_{4.3-x}\text{Co}_x\text{Mn}_{0.4}\text{Al}_{0.3}$ with $x = 0, 0.25, 0.50, 0.75$ and 1.0 , and crystalline structure of CaCu_5 [28]. The annealing must minimise the mechanic and crystalline dislocation and defects. That is necessary to form perfect ingot electrodes, in particular without cracking, neither crevasse.

The sample ingot electrodes are prepared from $\text{LaNi}_{4.3-x}\text{Co}_x\text{Mn}_{0.4}\text{Al}_{0.3}$ materials, formed as a cylinder with diameters $0.2\text{--}1\text{ cm}$, thickness $0.1\text{--}0.5\text{ cm}$. The electrodes are contacted and covered securely by epoxy resin, then subsequently polished using abrasive papers of grade 600, 800 and 1000. After polishing, the ingot

electrodes surface was several times cleaned, washed and dried.

Electrochemical cell is a standard system of three electrodes, working electrode (WE) is the above mentioned ingot electrodes, referent electrode (RE) is saturated calomel electrode (SCE), and counter electrode is platinum mesh. Working and counter electrodes are dipped in 6M KOH solution. The referent electrode is connected with solution by KCl-bridge and intermediate vessel containing $\text{KOH } 6\text{M}$ 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. To control measurement process, a PC with special software is used for controlling the system, collecting and analysing information of electrochemical impedance measurement.

The impedance analyses base on the variation of Z_r according to the frequencies in the interval 10 kHz to 0.01 Hz , and capacitance C calculated from imaginary part Z_i . The effect of frequencies, applied potential and Co contents are taken into consideration at the same time.

RESULT AND DISCUSSION

The Nyquist plots of impedance of the ingot electrodes with the different Co ratios x and at given polarisation potentials are presented in figure 1.

It is clear that the impedances spectra are modified semicircles, meaning only one time constant RC with certain dephasing, lowering the centre of the impedance loops [21].

The variation of real part Z_r as a function of frequency in log scale (figure 2) has been examined [27]. At middle and low frequencies, the Z_r values are evidently dependent on the Co ratios. For the Co ratio $x = 0.5$ and 0.75 at $E = -0.9\text{ V}$, Z_r are very approximate and together reaches the smallest values for all applied

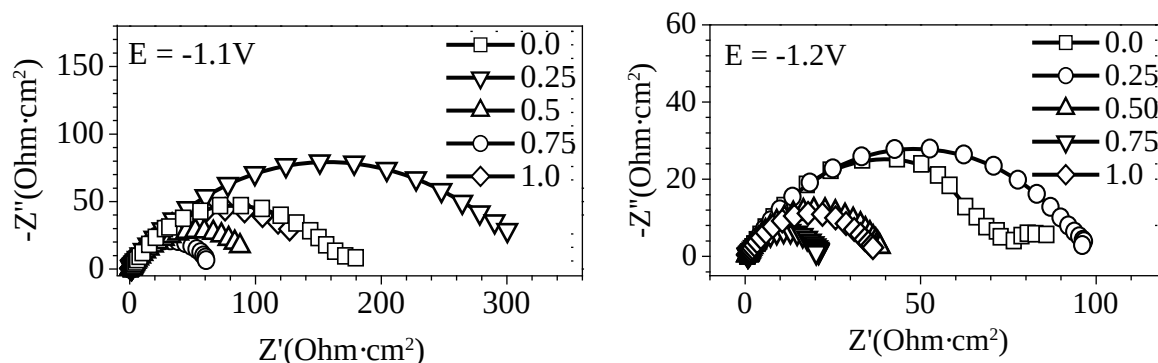


Fig. 1. Nyquist plots of electrochemical impedances of the LaNi_5 based ingot electrodes at different applied potentials and Co ratios x .

frequencies range. However, at $E = -1.2$ V variation of Z_r at $x = 0.5$ is different of that at $x = 0.75$. There is an alternative exchange of the smallest values between them. The real measured resistances at $x = 0, 0.25$ and 1 are always the highest for entire frequencies range.

The Co ratio $x = 0.75$ seems the most suitable for the electrochemical hydrogenation / des-hydrogenation on the ingot electrodes, corresponding to the previous results of space charges studies by EIS technique [22, 23], and the others [24–26]. At $x = 0.75$ the space charges quantity at internal side of the interface solid/liquid achieves minimal values [22, 23], corresponding to the high reaction rate of hydrogen redox, or to the low kinetic charge transfer resistance R_{ct} [27].

At each frequencies in range 10 kHz– 10 Hz, for a simple equivalent RC parallel circuit, capacitance C can be calculated as $C = 1/\omega Z_i$ [22]. Variations of capacitances C at applied frequencies f as a function of Co ratios x are presented in figures 3–5.

It is evident that at applied potentials $E = -0.9$ V, C achieves a maximum at Co ratio $x = 0.75$ for the

entire range of frequencies 10 Hz to 10 kHz. However, at $E = -1.0$ V the maximum is found at $x = 0.75$ only at high frequencies, and it changes to $x = 0.5$ at low frequencies (figure 4), the transition frequency is graphically 451 Hz. With $E = -1.1$ V (figure 5), the capacitance variation is the same, and transitional frequency is 1913 Hz. The transitional frequencies are tendentious to moves from low to high frequencies with increasing polarisation. At high polarisation, the maximum of the capacitance is completely displaced to Co ratio $x = 0.5$ (figure 6).

It is interesting that there are only two capacitances at Co ratio $x = 0.5$ and $x = 0.75$ which vary strongly with both frequency f and polarisation potential E . At the other Co ratios, the capacitance is found very stable, its variation is negligible in comparison with those at $x = 0.5$ and 0.75 (figures 3–6).

The displacement of the transitional frequencies can be manifested by ratio of capacitances $R = C_3/C_4$ of the samples $M3$ and $M4$ with $x = 0.5$ and 0.75 , respectively. If $R = 1$ there exists one transition fre-

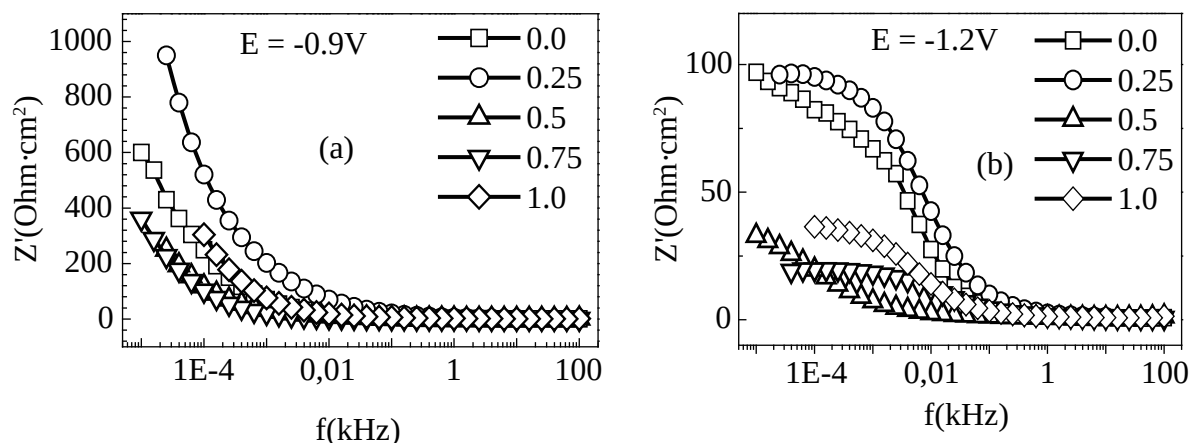


Fig. 2. Variation of Z_r as a function of log scale frequencies: at $E = -0.9$ V (a), and -1.2 V (b), inserted numbers are Co ratio x .

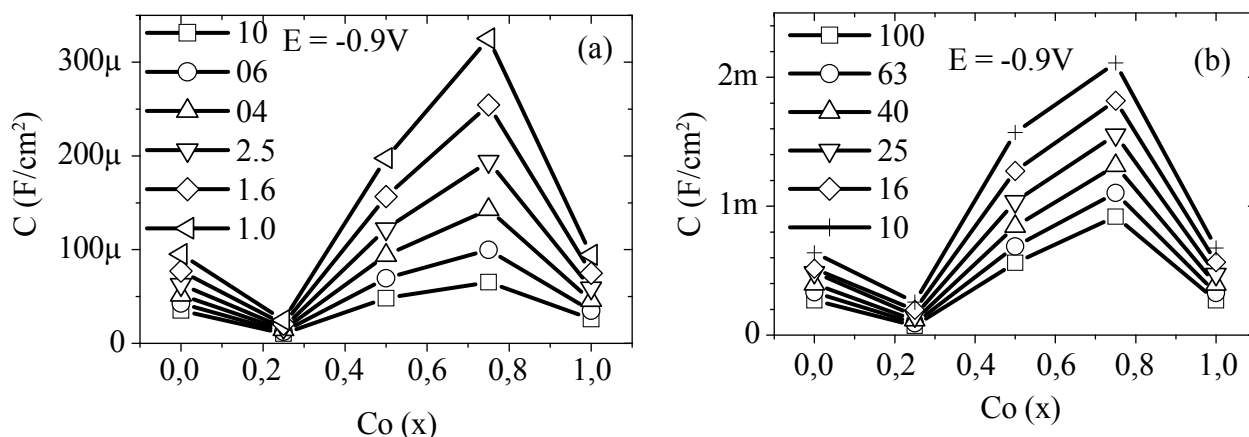


Fig. 3. Variation of capacitance C as a function of Co ratios x , $E = -900$ mV, $f = 1$ – 10 kHz (a), $f = 10$ – 100 Hz (b), inserted numbers are the applied frequencies.

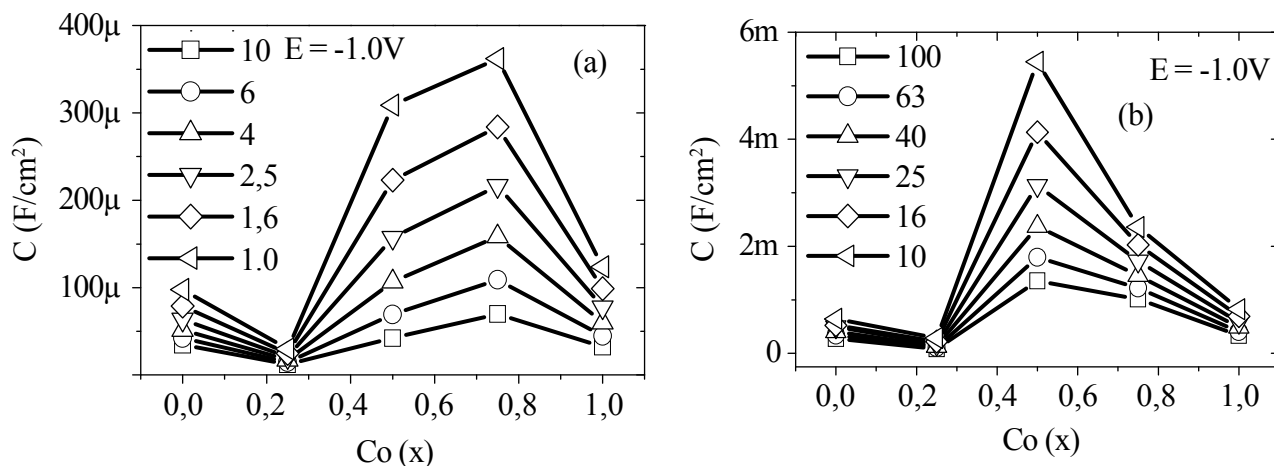


Fig. 4. Variation of capacitance C as a function of Co ratios x , $E = -1000\text{mV}$, $f = 0.1\text{--}10\text{ kHz}$ (a), $f = 10\text{--}100\text{ Hz}$ (b), inserted numbers are the applied frequencies.

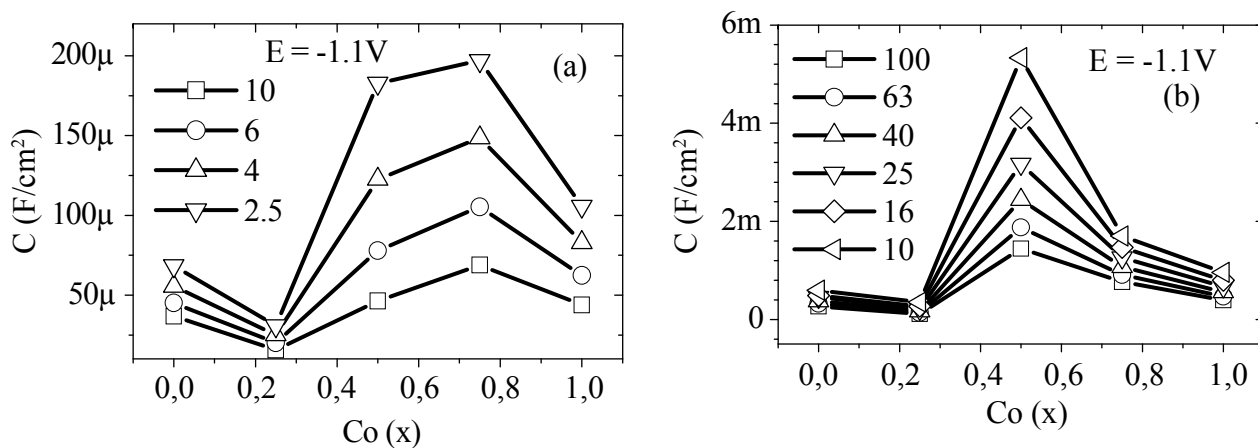


Fig. 5. Variation of capacitance C as a function of Co ratios x , $E = -1100\text{ mV}$, $f = 0.1\text{--}10\text{ kHz}$ (a), $f = 10\text{--}100\text{ Hz}$ (b), inserted numbers are the applied frequencies.

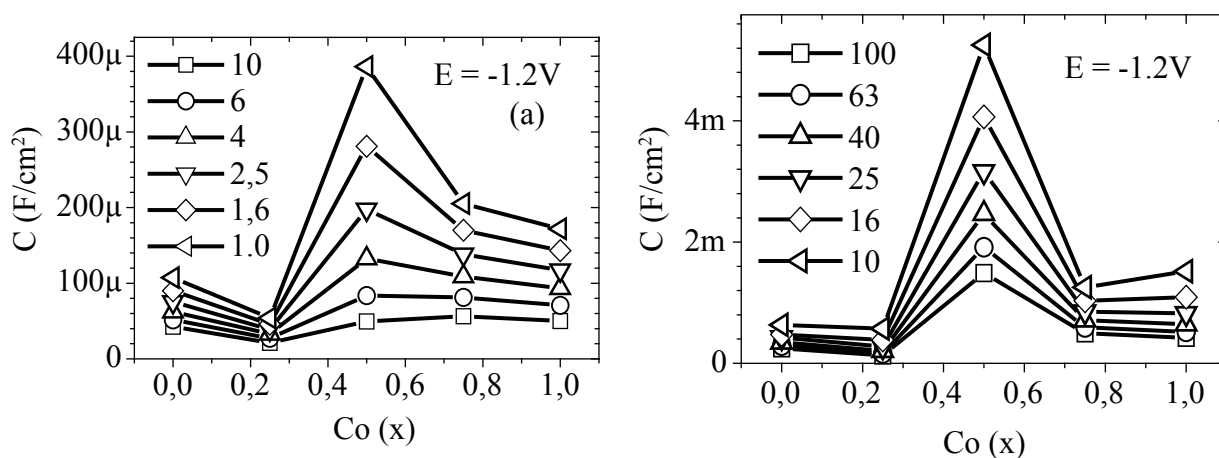


Fig. 6. Variation of capacitance C as a function of Co ratios x , $E = -1200\text{ mV}$, $f = 0.1\text{--}10\text{ kHz}$ (a), $f = 10\text{--}100\text{ Hz}$ (b), inserted numbers are the applied frequencies.

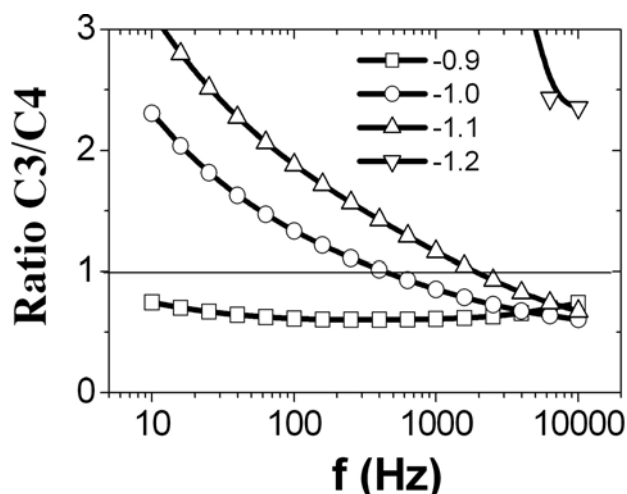


Fig. 7. Variation of ratio $R_C = C_3/C_4$ as a function of frequencies f (10 Hz–10 kHz): $R_C < 1$, $C_3 < C_4$, $x = 0.75$ is better; $R_C = 1$, $C_3 = C_4$ transition point; $R_C > 1$, $C_3 > C_4$, $x = 0.5$ is better.

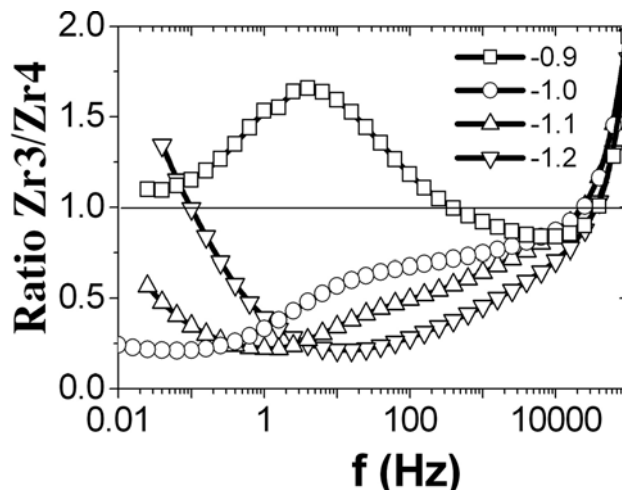


Fig. 8. Variation of ratio $R_{Zr} = Zr_3/Zr_4$ as a function of frequencies f (10 Hz–10 kHz): $R_{Zr} > 1$, $Zr_3 > Zr_4$, $x = 0.75$ is better; $R_{Zr} = 1$, $Zr_3 = Zr_4$ transition point; $R_{Zr} < 1$, $Zr_3 < Zr_4$, $x = 0.5$ is better.

quency. The variation of the ratio R is presented in figure 7. Analogously for Zr , the ratio $R_{Zr} = Zr_3/Zr_4$ represents relative reaction rate of the hydrogen redox (figure 8).

Criterion for the choosing the most suitable Co ratio is just the highest capacitance C and the lowest real part Zr of impedance. The results of the analysis are presented in table 1.

The frequencies effect seemly concerns also the suitable Co contents which is not too simple as it has been considered up to now [27]. Synthesising the results of analysis of C and Zr variation, it is evident that the suitable Co ratio is not unique as considered previously, but that depends on the polarisation and measurement signals frequencies.

At $E = -0.9$ V the most suitable Co ratio is $x = 0.75$, in spite of frequency range. At $E = -1.0$ and -1.1 V there exist so called transition region of frequency for

a displacement of Co ratio x from 0.75 to 0.5. This phenomenon suggests an existence of two electrically active matters. The first is 'fast' and the other 'slow', at the middle polarisation potentials. Both matters concern the Co content ratio x , seemly only appear evidently at $x = 0.5$ and $x = 0.75$. At high polarisation (-0.9 V or -1.2 V), both fast and slow matters similarly respond to the impedance signals.

It is found here also a different manifestation between the capacitance and the real impedance part. The transition evidently manifests between C values at high and low frequencies, but not evident between Zr for which should exist at least a one transitional polarisation between -0.9 V and -1.0 V. At $E = -1.2$ V the most suitable Co ratio is $x = 0.5$ for entire frequency range for capacitance C and Zr (table 1).

In practice, Ni-MH batteries can work under different regimes, including fast discharge or fast charge with high rate in order of some C . For the low rate process, the rate of charge-discharge can be $C/5$ or smaller. The working regime, in particular the rate of charge or discharge, affects evidently the lifetime of the batteries and their performance. It has been considered that the possibility to work at high rate ($> C$) could relate to a quick response to the impedance signals at high frequencies.

CONCLUSION

Electrochemical impedance studies of the Co contents effects have been carried out on the ingot electrodes of $\text{LaNi}_{4.3-x}\text{Co}_x\text{Mn}_{0.4}\text{Al}_{0.3}$ materials, with $x = 0, 0.25, 0.50, 0.75$ and 1.0 . The impedance data have been

Table 1. The most suitable Co ratios x at different frequencies ranges according to criterion 'highest capacitance C and lowest real resistance Zr '

Potentials E (V)	high f		1913 Hz		451 Hz		low f	
	C	Zr	C	Zr	C	Zr	C	Zr
-0.9	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
-1.0	0.75	0.5	0.75	0.5	trans	0.5	0.5	0.5
-1.1	0.75	0.5	trans	0.5	0.5	0.5	0.5	0.5
-1.2	0.5	0.5	0.5	0.5	0.5	0.5	0.5	—

analysed according to the impedance signal frequencies and applied polarisation potentials.

The result shows that there are two suitable Co ratios, the first is $x = 0.75$ for discharge process at -0.9 V and the other is $x = 0.5$ for the charge process at -1.2 V.

There exists a transition polarisation region, as applied potential $E = -1.0$ and -1.1 V, and transitional frequencies region for the passage of suitable Co ratios from $x = 0.75$ to 0.5 . The transitional frequencies increase according to the polarisation. That transition suggests certainly an existence of fast and slow matters in the interface electrode/electrolyte. The existence of both matters could be correlated to the Co ratio x . At high polarisation on both sides of the open circuit potential E° , $E = -0.9$ V and -1.2 V, there is no more transition, either of polarisation, neither of frequencies.

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