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DETERMINATION OF SURFACE CAPACITY Q_S AND SUPERFICIAL ACTIVE LAYER THICKNESS d_S OF $LaNi_5$ BASED INGOT ELECTRODES

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Abstract. $LaNi_{4,3-x}Co_xMn_{0,4}Al_{0,3}$ materials ($x = 0, 0.25, 0.5, 0.75, 1.0$) were prepared and examined using XRD technique. Ingot electrodes were formed from these materials for electrochemical studies, namely cyclic voltammetry with different scanning rates n (mV/s). A determination of surface capacity Q_S of the ingot electrodes was carried out with an extrapolation to infinite scan rate, taking into account the polarisation direction as charging or discharging. The thickness of superficial active layer d_S was calculated from Q_S values. Based on the variation of Q_S and d_S according to variation of Co ratio x, it is found that there are two suitable Co ratios corresponding to two opposite processes: charging and discharging.

Keywords: $LaNi_5$ materials, surface capacity, active layer thickness, Co content.

INTRODUCTION

Nickel-metal hydride (Ni/MH) batteries are the most suitable electric source for mobile devices, such as electronic instruments, hand-held computers, mobile phones, especially they are the most promising source of electric power for green vehicles. The most important development of the batteries in the recent decade is the increase in the capacity and lifetime of the negative materials. Nowadays, international effort is concentrated to find suitable $LaNi_5$ based materials with high capacity, long lifetime, good stability and reliability, but low cost. Some authors have studied the possibility to partially substitute Ni with other elements [1—5], others look for rare earths instead of La [1, 6—8], and many other practical variants [9—13].

However, in almost all electrochemical kinetic and mechanistic investigations of the $LaNi_5$ based materials, the working electrodes have been prepared in nearly the same ways. The powder of materials in the order of μm is mixed with additives, as binder and conductor, and then the mix is compressed into pellets with Ni foams as mechanical supports. In this case, the morphology and geometry of the electrodes active surface could not be exactly determined. The effective surface of the electrode is roughly hundreds of cm^2, and the current hence is very high, that is not usually suitable for kinetic and mechanistic studies, exclusive of the additives secondary effects. These disadvantages can be eliminated by replacing with ingot electrodes (InE).

One of the most significant advantages of ingot electrodes is the possibility to dearly define the surface, as its geometry and morphology, and consequently InE is practically suitable to study surface electrochemical phenomena. Meanwhile, in general, the electrode material surface properties have a deciding role for the kinetics of electrochemical processes. That is in particular significant for electrodes materials research in NiMH batteries. However, there are only some papers mentioning the application of ingot electrodes for materials research in Ni-MH batteries [14, 15]. In a recent paper ingot electrodes of $Zr_{0.5}Ti_{0.5}V_{0.6}Cr_{0.2}Ni_{1.2}$ alloys have been used to study the kinetics of hydrogen evolution reaction [15].

This paper focuses on studying the surface properties of $LaNi_5$ based ingot electrodes considering Co contents effects on the charging and discharging process.

EXPERIMENTTAL

$LaNi_{4,3-x}Co_xMn_{0,4}Al_{0,3}$ materials, with Co ratio varies from 0 to 1, were prepared by melting the materials at 1100 °C and were annealed at this temperature for 7 days to eliminate crevice, defects, and dislocation. Composition and crystalline structural analyses of the powdered materials were carried out using the XRD method and SEM.

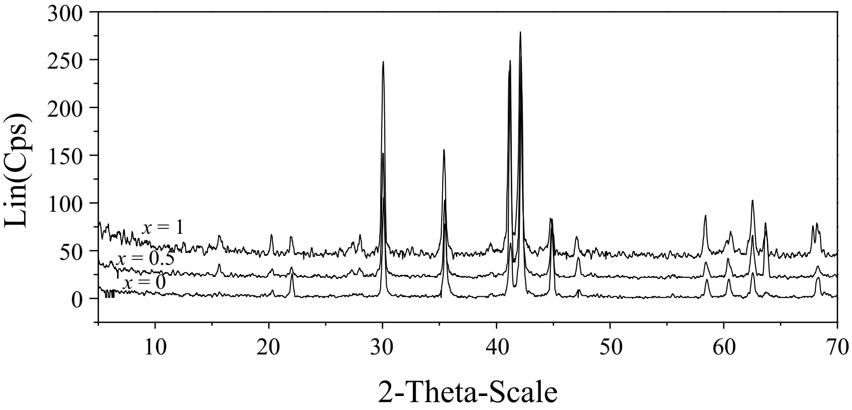

Fig. 1. XRD patterns of $LaNi_{4.3-x}Co_xMn_{0.4}Al_{0.3}$, $x=0$, $x=0.5$ and $x=1$

Ingot electrodes were formed from the above well-defined materials, with epoxy resin used as a resistant insulator. The surface of the ingot electrodes was polished consecutively by abrasive paper 600, 800 and 1000, then was washed and dried, and examined by SEM. The ingot electrodes were conserved in an exsiccator at room temperature before utilisation.

The electrochemical experiments were carried out in KOH 6M solution, using **AUTOLAB PGSTAT 30** equipped with software GPES and FRA controlling the measurement system and also analyses of the experimental CV and impedance data, respectively.

Ingot electrode were immersed into a solution of KOH 6M in a glass cell with a Pt coating electrode and 2 solution bridges to suppress the passage of KOH in to KCl compartment of saturated calomel electrode (SCE). After activation the electrode is sufficiently charged and then discharged using CV from Eo to –0.8V with different scan rates v, from 5 to 1000mV/s. The experiment was realised at room temperature. All chemicals are of analytic grades.

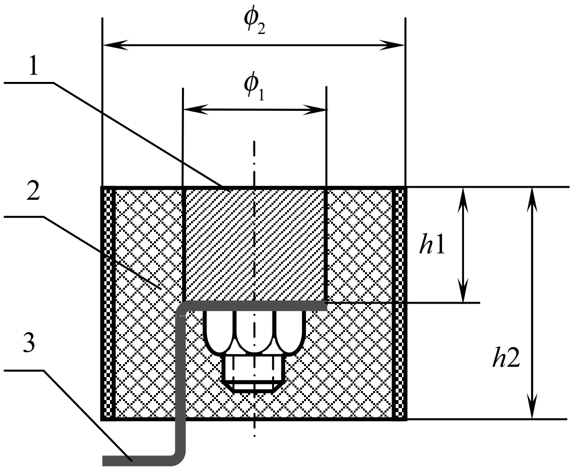

Fig. 2. Schema of ingot $LaNi_5$-type electrodes. *1* — $LaNi_5$ type materials, *2* — Epoxy resin, *3* — Copper wire contact

RESULTS AND DISCUSSION

Figure 1 presents the XRD patterns of the prepared materials with different Co ratios x. The results show that the chemical composition and crystalline structures of the materials are standard. Schema of the ingot electrodes is presented in figure 2.

As usual, $LaNi_{4.3-x}Co_xMn_{0.4}Al_{0.3}$ ingot electrodes are activated in order to get a stable charge-discharge process. The cyclic voltammogram of activation is presented in figure 3.

It is evident that the CV curves characterise the charge-discharge process of the negative electrode of Ni-MH batteries. The maximum currents of each activating cycle increase with cycle number and reach stable values after several tens of activating cycles.

1. INE SURFACE CAPACITY Q_S

For each CV cycle, the GPES software automatically calculates the charges quantity Q passed through the systems. However, Q depends on the CV rate v, and practically can be calculated by integral [16]:

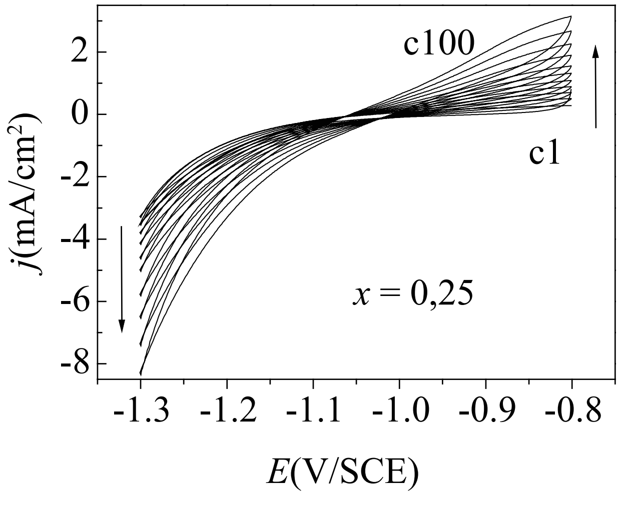

Fig. 3. Activating CV of the ingot electrode at Co ratio $x=0.25$, cycles c2 to c100, 10c separation, $v=10$ mV/s

$$Q(v)=\int i(E)dt=\alpha(\Delta E)\frac{1}{v} \qquad (1)$$

where $Q(v)$ is the charge quantity passed through the system at given scan rate v, E is polarisation potential depending on the scan rate v and α is an integral constant.

While v approaches infinite, $Q(v)$ approaches a limited value which is justly called the surface capacity Q_S. The surface capacity is evidently independent of any exterior factor such as scan rate v. However, it depends on the nature of the electrode and in addition of the other experimental condition. One can distinguish the surface capacity of charging Q_{CS} and of discharging Q_{DS} [17]. The variation of Q_{CS} and Q_{DS} as a function of Co ratios x, $x=0.0$ to 1.0, is represented in figure 4.

It is evident that the surface capacities Q_{CS} and Q_{DS} firstly increase with Co ratios and then decrease at the highest Co ratios. For $x=0.0$ to 0.5, both surface capacities are small and seem to be equal to each other. That means in this region where $x \leq 0.5$ there is no difference of the Co content effect between charging and discharging processes, and the effect is not remarkable. It is clear that at $x=0$ Q_S is very small, around 10^{-2} mC/cm^2 in comparison with the Q_S at other Co ratios of x. It seems that the presence of Co provides a remarkably larger surface capacity Q_S because of its catalytic effect for the surface activation and hydrogenation/dehydrogenation.

Both capacities Q_{CS} and Q_{DS} achieve maximum values, but not at the same Co ratio. For the charging process, corresponding to the more negative potential region, the maximum value occurs obviously at $x=0.5$, and for the discharging process forward to the more positive polarisation, at $x=0.75$. After achieving the maximum, both capacities decrease and separate from each other. Their absolutely biggest difference occurs at $x=1.0$ $\Delta Q=|Q_{CS}-Q_{DS}|=0.15$.

The difference of the capacities ΔQ can be considered as a degree distinguishing the effect of Co contents on the two opposite processes: charging and discharging. Variation of ΔQ as a function of Co ratio x is graphically presented in figure 5. It is helpful to note that at $x=0.5$ the difference is minimal $\Delta Q=0.006$ and the ratio is nearly at unity $RQ=Q_{CS}/Q_{DS}=1.01$ (however, at $x=0$ $\Delta Q=0.011$, while $RQ=5$), (figure 5). Hence, it seems that exclusive $x=0.5$ causes no effect difference on the two opposite, charging and discharging, processes.

2. ACTIVE LAYER THICKNESS D_S

In the charge-discharge processes the highest rate reaction of hydride formation / deformation takes place at the electrode surface region. The rate of this reaction is so high as to be independent of the scan rate v of the polarisation. This critical surface reaction provides the superficial capacity Q_S. Studying and finding out the depth of the active surface layer will be significant not only for the fundamental aspect but also for technological application of the electrode materials, especially for the development of new efficient electrode materials. However, it is a fact that using the compressed powdered materials electrodes, mechanistic electrochemical studies on the materials superficial parameters, such as thickness of the surface-active layer, become obviously impossible.

In this part, surface capacity Q_S values, determined from CV data and using specific hydrogenation properties of $LaNi_5$, have been exploited in order to calculate the depth of the active surface film. Surface capacity Q_S represents justly a quantity of atomic hydrogen present in hydride state, as $LaNi_5H_y$, on the electrode surface [16, 17]. However, $LaNi_5$ alloy can absorbs hydrogen to form hydride with relative maximum ratio of $R_H=H/LaNi_5=6$ ($y=6$) [18]. Hence, one can easily estimate the minimal thickness of the surface-active

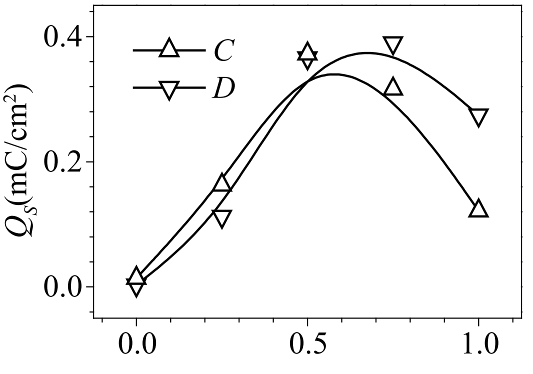

Fig. 4. Variation of Q_{CS} and Q_{DS} as a function of Co ratios x

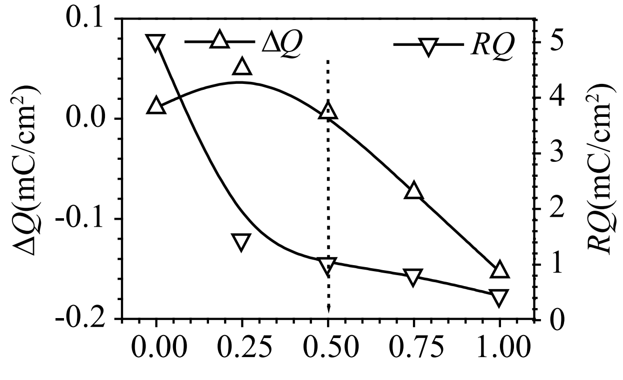

Fig. 5. Variation of difference $\Delta Q=Q_{CS}-Q_{DS}$ and ratio $RQ=Q_{CS}/Q_{DS}$ as a function of Co ratios x

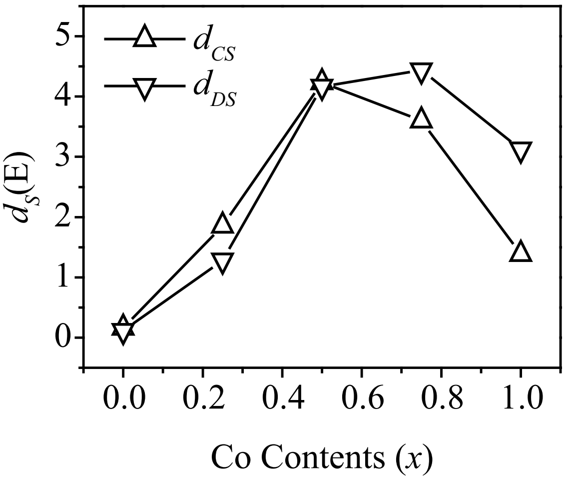

Fig. 6. Variation of minimal thickness of surface-active later d_S as a function of Co ratios x d_{CS}: determined from Q_{CS} d_{DS}: determined from Q_{DS}

layer d_S from Q_S data (figure 6). It is evident that, for a constant Q_S, if $R_H < 6$ the calculated thickness d_S will be higher than those presented in figure 6.

At $x = 0$ and 0.25, d_S seems anomalously small. However, there are practically active centres on the surface, and the quantity of those centres decides the surface capacity Q_S. It is obvious that for $x = 0$ there exists only a small number of surface active centres, giving consequently a small Q_S.

Different from bulk materials, the active surface layer contributes its catalytic effect for the hydrogenation / dehydrogenation. The layer has a role of transitional film for the displacement of H from the bulk hydride to a surface hydride (if exists) and finally to the absorbed hydrogen surface before H being discharged there on the interface electrode/solution. However, the active surface thickness must be closely correlated to the charging and discharging capabilities at extremely high CV rate. As presented in figure 6, the depth depends strongly on the Co ratio, and achieves around 4Å at $x = 0.5$ for the charging process and at $x = 0.75$ for the discharging one. The depth 4Å corresponds about two single atomic layers. However, at the others Co ratios, the thickness strongly decrease, in particular for $x = 0$ and $x = 1.0$.

CONCLUSION

Ingot electrodes are useful to study the electrochemical surface properties of $LaNi_5$ based materials, especially superficial phenomena with fast response during charge-discharge processes. Ingot electrodes were formed from $LaNi_{4,3-x}Co_xMn_{0,4}Al_{0,3}$ materials ($x = 0.0$—1.0) for studies of Co content effect. Surface capacity Q_S and superficial active layer thickness d_S of the ingot electrodes were determined. Both parameters depend strongly on the Co content ratio x.

Based on the variation of Q_S and d_S as a function of the Co content ratio x, it is supposed that there are active centres on the electrode surface, and Co additive increases a number of those centres. The bigger Q_S, the larger number of the active centres is. Hence the effect of Co additive can be studied via the surface capacity Q_S.

The value of Q_S and of d_S were taken as a criterion for choosing the suitable Co ratio x. There are two highest values of Q_S and d_S corresponding to charging and discharging processes. Those values indicate two suitable Co ratios, one is $x = 0.5$ for the charging process, and the other for discharging is $x = 0.75$.

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