Thermal behaviour of Ni–Mn layered double hydroxide and characterization of formed oxides

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Abstract
Thermal behaviour of the Ni–Mn layered double hydroxide (LDH) with Ni/Mn molar ratio equal to 2 prepared by coprecipitation was studied in temperature range 200–1100°C by thermal analysis (TG/DTA/EGA), powder X-ray diffraction (XRD), infrared spectroscopy and voltammetry of microparticles. A loss of interlayer water (dehydration) and sample decomposition accompanied by H2O and CO2 evolution were observed at 175 and 265°C, respectively. Thermal decomposition of Ni–Mn LDH resulted in formation of a predominantly amorphous mixture of oxides. A relatively high content of amorphous part was observed in samples heated at 200–500°C. The onset of Ni6MnO8 crystallization was detected by XRD in samples heated at 300°C. Together with Ni6MnO8, NiMnO3 was detected by XRD in samples heated at 500°C. According to the voltammetry, the further reconstruction of oxides took place above 600°C. NiMnO3 and Ni6MnO8 were converted to spinel (Ni,Mn)3O4 occurring together with NiO. These oxides were observed in diffraction patterns of samples heated at high temperatures (800–1100°C).

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1. Introduction
Hydrotalcite-like compounds, a class of layered double hydroxides, can be represented by the general formula [MII1−xMIIIx(OH)2]x+[An−x/n]·yH2O where MII and MIII are divalent and trivalent metal cations, An− is an n-valent anion and x has usually values between 0.25 and 0.33. Their crystal structure is similar to that of brucite—Mg(OH)2 where each Mg2+ ion is octahedrally surrounded by six OH− ions and the different octahedra share edges to form infinite sheets. The sheets are stacked one on top of the other and are held together by weak interactions via hydrogen bonds. In the hydrotalcite-like compounds, the MII/MIII isomorphous substitution in octahedral sites of the hydroxide (“brucite”) sheet results in a net positive charge which is neutralized by the interlayers composed of anions and water molecules. Hydrotalcite-like compounds as well as products obtained by their thermal treatment have found many practical applications such as catalysts or catalyst precursors, ion exchangers, adsorbents, and polymer stabilizers [1–3].

A large number of layered double hydroxides with a wide variety of MII and MIII metal cations in hydroxide layers was prepared and reported in the literature. However, only a few papers reported on hydrotalcite-like compounds containing manganese. The naturally occurring Mg–Mn layered double hydroxide, desautelsite, was described by Dunn et al. [4]. Hansen and Taylor [5] prepared the Mg–Mn layered double hydroxide by air oxidation of MnCO3 suspended in Mg(NO3)2 solution at constant pH ∼ 9 and also by coprecipitation of Mg(NO3)2 and MnCl2 solution in strongly alkaline conditions. Fernandez et al. [6] studied the thermal stability of Mg–Mn hydrotalcite-like compound prepared by the coprecipitation method. According to the temperature programmed reduction results, the main part (84%) of Mn2+ was oxidized to Mn3+ during the synthesis. Barriga et al. [7] described the preparation and characterization of Ni–Mn hydrotalcite-like compounds with Ni/Mn molar ratios close to 2 and 3. Thermal behaviour of these compounds was also reported.
Nickel-based layered double hydroxides were studied as perspective electrode materials. They are isostructural with \( \alpha \)-nickel hydroxide, the positive electrode material of Ni-based alkaline secondary cells. The \( \alpha \)-Ni(OH)\(_2\) behaves as an hydrotalcite-like anionic clay and it is able to exchange the intercalated anions for hydroxyl ions from the alkaline electrolyte [8]. The partial isomorphous substitution of Ni\(^{II}\) with a suitable trivalent cation (e.g. Al, Fe, Co, Cr, and also Mn) can stabilize \( \alpha \)-Ni(OH)\(_2\) due to an increase of the positive charge on the hydroxide layers [9–11]. The coprecipitation of solutions containing Ni\(^{2+}\) and Mn\(^{2+}\) in alkaline mixture of NaOH and Na\(_2\)CO\(_3\) solutions were used for preparation of these materials. H\(_2\)O\(_2\) was added into metal cations containing solution to oxidize Ni\(^{II}\) to its higher oxidation states.

Considering that Mn is able to attain variable oxidation states, it is interesting not only as a component of power sources but also as an effective component in mixed oxide based catalysts suitable for oxidation and combustion reactions [12]. Many mixed oxide based catalysts can be obtained by the controlled thermal decomposition of hydrotalcite-like precursors [1–3]. These catalysts usually show a large surface area, high metal dispersion and stability against sintering. In the presented work, the thermal behaviour of Ni–Mn layered double hydroxide with Ni/Mn molar ratio equal to 2 is studied. The thermal decomposition of starting Ni–Mn layered double hydroxide and phase transitions during its heating are reported. Thermal analysis, X-ray diffraction, infrared spectroscopy, surface area measurements, chemical and elemental analysis and voltammetry of microparticles are used for description of these processes and characterization of oxides formed during heating.

2. Experimental

2.1. Preparation of samples

Ni–Mn layered double hydroxide was prepared by coprecipitation. An aqueous solution (450 ml) of Ni(NO\(_3\))\(_2\)·6H\(_2\)O and Mn(NO\(_3\))\(_2\)·4H\(_2\)O with Ni/Mn molar ratio equal to 2 and total metal ion concentration of 1.0 mol\(\cdot\)l\(^{-1}\) was added dropwise into 200 ml of 0.5 M Na\(_2\)CO\(_3\) solution under vigorous stirring. During the synthesis, the temperature was maintained at 20°C and pH at about 10 by a simultaneous addition of 3 M NaOH. The addition of both solutions took 1 h. The resulting suspension was then maintained at 20°C with stirring for 18 h. The product was filtered off, washed several times with distilled water and dried at 60°C in air. The dried product was heated at chosen temperatures in the range 200–1100°C in air for 2 h and then cooled to the room temperature. These heated samples were used for the XRD, IR, EPR, voltammetric and surface area measurements.

Reference oxides NiMnO\(_3\), Ni\(_8\)MnO\(_8\), and (Ni,Mn)\(_3\)O\(_4\) were prepared by evaporation of Ni\(^{II}\) and Mn\(^{II}\) nitrates with citric acid dissolved in minimum amount of water similarly as described by Grygar et al. [13,14]. Based on report of Feltz and Töpfer [15], the heating temperature 650°C was chosen for preparation of NiMnO\(_3\) and Ni\(_8\)MnO\(_8\) and 800°C for preparation of (Ni,Mn)\(_3\)O\(_4\). The prepared oxides were used as reference samples for voltammetry and chemical analyses.

2.2. Experimental techniques

Thermal analyses, including thermogravimetry (TG), differential thermal analysis (DTA) and evolved gas analysis (EGA), were carried out using a Netzsch STA 409 instrument equipped by the quadrupole mass spectrometer QMS 403/4 (Balzers) for analysis of gases evolved during sample heating. The heating rate of 10°C\(\cdot\)min\(^{-1}\) in air or argon with flow rate of 75 ml\(\cdot\)min\(^{-1}\) and 50 mg of sample were used. The furnace and mass spectrometer were connected by stainless steel capillary of internal diameter 0.1 mm heated to about 200°C to prevent the condensation of evolved gases. Gaseous products were continually monitored for chosen mass numbers \(m/z\) (18—H\(_2\)O\(^+\), 44—CO\(_2\)\(^+\) and 16—O\(^+\)).

Powder X-ray diffraction patterns were recorded using a Seifert XRD 3000P instrument with Co \(K\alpha\) radiation (\(\lambda = 0.179 \text{ nm}, \text{graphite monochromator, goniometer with Bragg–Brentano geometry}\) in 2\(\theta\) range 12–75\(^\circ\), step size 0.05\(\circ\). Raylex software and PowderCell 2.4 were used for phase identification and quantitative analysis, respectively. PowderCell is based on fitting of the experimental diffractograms to the patterns generated from the crystal structures of the components by refining their scale factor (recalculated to the percentages by the programme), lattice parameters, and diffraction line profile functions. The structural models were adopted from the Inorganic Crystal Structure Database (FIZ Karlsruhe, Germany).

Fourier-transform infrared absorption spectra were recorded using the KBr pellettechnique on the spectrometer Nicolet Avatar 320 in the range 4000–400 cm\(^{-1}\) and the resolution of 4 cm\(^{-1}\).

Surface area measurements were carried out by nitrogen adsorption at 77 K using Beckmann Coulter SA 3100 equipment and evaluated by one point BET method.

Electron paramagnetic spectra (EPR) were obtained with powdered samples placed in quartz ampoules (diameter 4 mm) at laboratory temperature using spectrometer ELEXYS (Bruker-Biospin GmbH, Germany). Mn(II)/ZnS provided by Galenus GmbH (Germany) was used as a reference.

For voltammetry of microparticles, the powdered samples were mechanically deposited on the surface of paraffin impregnated graphite rod. Potentials were measured against saturated calomel reference electrode (SCE). Voltammetric curves were measured from the open circuit potential (i.e. equilibrium potential) toward negative potentials at scan rate 1 mV\(\cdot\)s\(^{-1}\).

The chemical composition of the samples was determined by AAS after sample dissolution in hydrochloric acid. The average error of the determination was about 3% rel. The
metal ions redox state was determined by iodometry or by permanganometric back-titration after sample dissolution in an acidified solution of Mohr salt. Iodometry (i.e. dissolution in excess KI in cold diluted HCl) is more convenient, but it was only applicable in samples obtained at lower calcination temperatures (< 600°C). The less reactive calcines obtained at higher temperatures had to be dissolved in diluted H₂SO₄ and H₃PO₄ under heating in N₂ atmosphere with stirring and ultrasonication. The methods yielded the same results within a common error of estimation (3–5% rel.). In both these redox analyses, Mn³⁺, Mn⁴⁺, and Ni³⁺ ions could be determined. The results were expressed as an average formal Mn and/or Ni valence.

An easily dissolving part (considered to be amorphous) of samples was determined by the dissolution of sample in a mixture of acetic acid and hydrazine hydrochloride. 50 mg samples were dissolved at room temperature with stirring in 50 ml of solution containing 5% CH₃COOH and 5% N₂H₄·HCl. Reaction mixture was sampled in chosen time intervals (2, 5, 10, 20, and 40 min, respectively). The solid part was filtered off and Ni and Mn concentrations in solution were determined by AAS. In contrast to the XRD crystalline species, the most reactive components of the oxide mixtures were completely dissolved very quickly (i.e. in the first few minutes). The content of the amorphous components in the samples was estimated by following way: the data from dissolution experiments were fitted to a parabolic function and the dissolved part at the start of reaction (i.e. at the time \( t = 0 \)) was evaluated from the intersection of this function with the \( y \) ordinate.

3. Results and discussion

The following results were obtained by the chemical analysis of the dried product: (in wt%) Ni 34.4, Mn 16.1 and CO₂⁻ 7.44. The results confirmed the Ni/Mn molar ratio equal to 2. A well-crystallized hydrotalcite-like phase was present in the dried product and a trace amount of MnCO₃ (rhodochrosite) was also detected in the powder XRD pattern. During the coprecipitation, the main part of Mn²⁺ is oxidized to Mn³⁺ but the presence of some Mn²⁺ in coprecipitated samples was reported [6,7]. The Mn/CO₂⁻ molar ratio of 2.36 determined by chemical analysis in dried product was higher than theoretical value of 2, which should be expected when all manganese ions in hydroxide layers are present as Mn³⁺. Thus, a part of Mn in hydroxide layers might be Mn²⁺. The presence of Mn²⁺ in the dried sample was proved by EPR spectroscopy. On the other hand, the formal valence of Mn in the dried sample was evaluated as 3.22. This fact indicated that some Mn in the sample had to be in the valence 4⁺ (e.g. a formation of amorphous MnO₂ could be considered). The non-integer Mn formal valence in the dried sample was a result of Mn³⁺, Mn⁴⁺ and Mn⁴⁺ combination and an evaluation of the LDH charge density seems to be uncertain.

Other authors [16–19] reported the thermal behaviour of hydrotalcite-like compounds. The following main processes can be observed during the hydrotalicates heating: release of interlayer water, thermal decomposition followed by formation of oxides, and finally spinel crystallization.

During the heating in the temperature range 100–400°C, two endothermic effects accompanied by the H₂O and CO₂ evolution were observed on the DTA curves (see Figs. 1 and 2). The first one observed at 175°C was ascribed to the release of interlayer water. The presence of CO₂ in gases evolved at low temperatures (up to 200°C) can be explained by the release of carbon dioxide adsorbed at the sample surface and/or by the partial decomposition of rhodochrosite. The second DTA effect observed at 265°C was raised by the dehydroxylation of hydroxide layers and decomposition of interlayer carbonate anions. The simultaneous evolution of H₂O and CO₂ was detected at this temperature. The results of TG and DTA measurements corresponding to the sample dehydration and decomposition obtained both in air and argon close resembled. The subsequent CO₂ evolution with maximum at 300°C (in air) or 350°C (in argon) was detected by EGA. This effect was ascribed to the rhodochrosite decomposition. A slight effect on the CO₂ evolution curve was also observed at ca. 520°C both in air and argon. It might be attributed to the decomposition of a residual carbonate.

Fig. 1. Thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA) and evolved gas analysis (H₂O and CO₂) results of Ni-Mn LDH measured in air.
Table 1
Surface area, chemical, elemental and phase composition of samples prepared by heating of Ni–Mn layered double hydroxide at various temperatures. The percentage of the residual CO\textsubscript{2} and H\textsubscript{2}O in the oxides is omitted

<table>
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<tr>
<th>Heating temperature (°C)</th>
<th>(S_{\text{BET}}) (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>Mn (wt%)</th>
<th>Mn valence (wt%)</th>
<th>Ni (wt%)</th>
<th>Ni valence (wt%)</th>
<th>Amorphous component (wt%)</th>
<th>Ni\textsubscript{2}MnO\textsubscript{8} (wt%)</th>
<th>NiMnO\textsubscript{3} (wt%)</th>
<th>(Ni,Mn)\textsubscript{2}O\textsubscript{4} (wt%)</th>
<th>NiO (wt%)</th>
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<td>0</td>
<td>36</td>
<td>64</td>
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Fig. 2. Thermogravimetry (TG), derivative thermogravimetry (DTG), differential thermal analysis (DTA) and evolved gas analysis (H\textsubscript{2}O, CO\textsubscript{2} and O\textsubscript{2}) results of Ni–Mn LDH measured in argon.

A gradual decrease of intensity of OH bands and splitting of CO\textsubscript{3}\textsuperscript{2-} bands with increasing calcination temperature were observed in IR spectra (Fig. 3). The presence of NO\textsubscript{3}\textsuperscript{-} in the dried product was also detected by IR spectroscopy but it disappeared completely at 400 °C. IR spectra of the samples heated at 400 °C and higher temperatures showed only lattice modes of formed oxides in the range 800–400 cm\textsuperscript{-1}.

The total weight loss of 30% up to 400 °C corresponded to the loss of entire amount of water (including both the de-hydration of the LDH interlayer space and dehydroxylation of the hydroxide layers) and carbon dioxide release. Thermal decomposition of the Ni–Mn hydrotalcite-like compound caused a considerable increase of its surface area (from 83 m\textsuperscript{2} g\textsuperscript{-1} for the dried sample to 125 m\textsuperscript{2} g\textsuperscript{-1} measured for the sample calcined at 300 °C). After reaching the maximum value at 300 °C, the surface area gradually decreased with increasing calcination temperature (see Table 1).
Fig. 4. Powder XRD patterns of Ni–Mn LDH heated at various temperatures (H: hydrotalcite-like phase, R: rhodochrosite, M: murdochite, Ni$_6$MnO$_8$, I: ilmenite, NiMnO$_3$, S: spinel (Ni,Mn)$_3$O$_4$, B: bunsenite, NiO).

Powder XRD patterns of samples heated at different temperatures are shown in Fig. 4. The samples heated at 200 and 300 °C were rather amorphous, heating at 400 °C resulted in highly disordered product (broad XRD reflections at $d \sim 2.4$ and 2.1 Å). Samples heated at 500 and 600 °C showed the crystallization of primary oxide phases—Ni$_6$MnO$_8$ (murdochite type compound exhibiting NaCl structure with cationic vacancies) and NiMnO$_3$ with ilmenite structure. These oxides were of medium crystallinity. The diffraction line corresponding to the (111) plane in Ni$_6$MnO$_8$ exhibited significantly higher intensity in comparison with other diffraction lines of this oxide. The preferential orientation of (111) plane in Ni$_6$MnO$_8$ could be connected with the arrangement of metal hydroxide layers with the (001) orientation in the hydrotalcite crystal structure and a change of the unit cell orientation. An onset of crystallization of spinel (Ni,Mn)$_3$O$_4$ was observed at 700 °C. The relatively small lattice parameter $a = 8.360$ Å was evaluated for this oxide, which crystallized together with NiMnO$_3$—ilmenite. The lattice parameter increased continuously to 8.399 Å at 1000 °C, approaching the values $a = 8.402$ Å and 8.380 Å reported for stoichiometric NiMn$_2$O$_4$ (PDF 74-1865) and Ni$_2$MnO$_4$ (PDF 36-0083), respectively. A similar relation between the spinel lattice parameters and the amount of cation vacancies (increased Mn valence) was well documented in the case of LiMn$_2$O$_4$ obtained at varying temperature [21].

The complete transformation of NiMnO$_3$ and Ni$_6$MnO$_8$ into (Ni,Mn)$_3$O$_4$ spinel and NiO (bunsenite) was observed at 800 °C. The transformation of oxide phases (probably accompanied by a release of oxygen) at temperatures above 700 °C was also indicated by the thermal analysis performed in air. A slight weight loss was observed in the temperature interval 735–790 °C on the TG curve, together with a clear endothermic effect with minimum at 765 °C on the DTA curve. These effects had not been detected, when the analysis was carried out in argon. On the other hand, a slight release of oxygen was observed in argon at ca. 670 °C. For the Ni–Mn hydrotalcite-like compound heated in air, Barriga et al. [7] reported the endothermic effect at 782 °C. They reported also a weak, broad, ill-defined exothermic effect centred at ca. 580 °C which was ascribed to an oxidation, e.g. Mn$^{III}$ to Mn$^{IV}$. Though such exothermic effect was not distinguished in the measured DTA curve, an oxidation of the sample during its calcination in air could be expected. Contrary to the study provided previously by Barriga et al. [7], the other oxide (i.e. Ni$_6$MnO$_8$ of murdochite type, which crystallized together with NiMnO$_3$—ilmenite) was found in the powder XRD patterns of samples calcined at 500–700 °C. Only spinel and bunsenite were detected in samples heated at high temperatures (900–1100 °C). The phase composition changing in the dependence on heating temperature is summarized in Table 1 and the lattice parameters of bunsenite, murdochite, and spinel-type components of the oxide mixtures in Table 2; both percentages and lattice parameters were evaluated applying PowderCell 2.4 programme (see Section 2).

EPR spectroscopy was used to characterize the coordination environment of Mn$^{2+}$ ions in the heated samples. The $g$ values of the main components of measured EPR spectra (Table 3) agreed with those reported for Mn$^{2+}$ in Mn-substituted Mg–Al layered double hydroxides and their calcination products [12] and Mn$^{2+}$ in Mn-oxides todorokite and hollandite [20]. In the starting Ni–Mn layered double
of cation-vacant bunsenite and it is also electrochemically inactive, probably due to a relatively low content of electrochemically active Mn$^{4+}$ cations substituting the inactive Ni$^{2+}$ ones in the oxide lattice. The reductive dissolution peaks of samples prepared by heating of Ni–Mn layered double hydroxide occurred at approximately three potentials: (i) the positive peaks C1 + C2 related to the dissolution of Mn$^{III,IV}$ oxides, probably with a low degree of substitution, (ii) the peak C3 + C4 close to 0 V and (iii) the negative peak C5. Both C3 + C4 and C5 peaks were probably related to the dissolution of Ni–Mn$^{III,IV}$ oxides with a substantial Ni content. The highly reactive, probably amorphous Mn$^{III,IV}$ species, which was responsible for the sharp C2 peak found in the samples heated at low temperatures, was gradually consumed due to the incorporation into Ni–Mn oxides as heating temperature increased (see Fig. 6). No such signal was observed in well-crystalline reference samples. The species responsible for the C2 peak could be present either on the surface of the particles of the major components or as separate particles; this cannot be distinguished by voltammetry. The measured voltammograms changed significantly in the region of peaks C3 to C5 in the samples heated at 500–700°C. This indicated a transformation of the oxides: the less reactive species present in the samples heated at low temperatures (C5 peak) was transformed to another with characteristic C3 peak after sample heating at 600°C. The voltammetric curve of sample heated at 600°C was very similar to that obtained for reference NiMnO$_3$ and the high content of NiMnO$_3$ in this sample was also confirmed by XRD. As the heating temperature increased, the C3 peak shifted to the more negative potentials (C4) and the general shape of the voltammetric curves adopted the shape characteristic for (Ni,Mn)$_3$O$_4$ spinels. The C1 + C2 peaks appeared in voltammograms of samples heated at temperatures higher than 900°C and developed to a well-defined symmetric peak when heating temperature was higher than 900°C. The shape of these voltammograms closely resembled that of the reference spinel oxides. These voltammetric results agreed with XRD and thermal analysis that confirmed the transformation of primary formed oxides (Ni$_6$MnO$_8$ and NiMnO$_3$) into spinel and bunsenite at 700–800°C.

The formal valences of metal ions (Ni and Mn) in samples were evaluated from the total amount of metals and the results of redox analysis performed by iodometry

Table 3
The g values of EPR spectral components. Intensity of the EPR signal is assigned as strong (s), medium (m), and weak (w)

<table>
<thead>
<tr>
<th>Heating temperature (°C)</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1.99 (s)</td>
<td>2.20 (s)</td>
<td>2.6–2.8 (w)</td>
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</tr>
<tr>
<td>200</td>
<td>1.99 (s)</td>
<td>2.21 (s)</td>
<td>2.95 (w)</td>
<td>6.3 (s)</td>
</tr>
<tr>
<td>300</td>
<td></td>
<td>ferrimagnetic samples</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400–800</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>2.09 (m)</td>
<td>2.20 (s)</td>
<td>2.73 (s)</td>
<td>&gt; 10 (w)</td>
</tr>
<tr>
<td>1000</td>
<td>2.08 (m)</td>
<td>2.20 (s)</td>
<td>3.25 (s)</td>
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<td>1100</td>
<td>2.08 (s)</td>
<td>2.23 (s)</td>
<td>2.90 (s)</td>
<td>&gt; 10 (w)</td>
</tr>
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</table>

Fig. 5. Voltammetry curves of reference oxides.

hydroxide (dried product) and samples heated at 200, 300, and 400°C, respectively, octahedral Mn$^{2+}$ was observed (species I and II). The presence of Mn$^{3+}$ in these compounds is not in a contradiction to the evaluated formal Mn valence higher than 3: especially in Mn$^{III,IV}$ oxides the non-integer formal valences are always a result of a combination of Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$. Surprisingly, Mn$^{4+}$ signal was absent although the mean Mn valence of 4 in the latter samples was determined. But also in the reports [12,20] Mn$^{4+}$ seemed to be EPR silent. The samples heated at 500–800°C were ferrimagnetic, likely due to the presence of the ilmenite-like phase NiMnO$_3$ and therefore it was impossible to acquire room temperature EPR spectra. In the samples composed of spinel and bunsenite obtained at temperatures above 800°C, Mn$^{2+}$ in tetrahedral coordination environment (A-site of the spinel lattice, g > 2.3, species III) was found beside the octahedrally coordinated Mn$^{2+}$ (g ~ 2.1, species I and II).

The voltammetric curves of reference oxides NiMnO$_3$ and (Ni,Mn)$_3$O$_4$ prepared by evaporation of Ni$^{II}$ and Mn$^{II}$ nitrates with citric acid showed well defined responses (Fig. 5). Bunsenite, NiO, was not included in the set of reference compounds, because it did not yield cathodic peaks of reductive dissolution and therefore it behaved as an inert compound. Murdochite-type Ni$_6$MnO$_8$ has a structure
Fig. 6. Voltammetry curves of Ni–Mn LDH heated at various temperatures.

or permanganometry. In samples calcined at 300, 400, and 500°C, respectively, the redox analysis data processing yielded all the Mn present in formal valence +4 and therefore Ni should be in valence higher than +2. As follows from the Table 1, the formal valences of Mn and Ni reached their maxima after sample heating at 300–500°C. At temperatures higher than 600°C, the formal valence of Mn decreased as the spinel composition changed from (Ni0.4Mn0.6)3O4+x to (Ni0.3Mn0.7)3O4+x at 1000°C. An excess of oxygen in spinels formed at temperatures below 1000°C could be expected, based on the determined Mn valence and decreased value of the lattice parameter with respect to the stoichiometric NiMn2O4.

The extracting system of acetic acid and hydrazine hydrochloride showed to be specific for the dissolution of the amorphous part of the calcined samples. The sample heated at 200°C was completely dissolved in several minutes, while NiMnO3, NiMnO4 and NiO oxides were practically intact within several hours. The spinels dissolved slowly, i.e. within tens of minutes to hours. All the samples obtained at temperatures below 700°C contained easily dissolving components, passing to the solution in a short time (1–3 minutes). The extracted amounts of Mn and Ni were re-calculated to the quantity of the amorphous fraction in the samples assuming the same Mn and Ni valences in the amorphous and crystalline parts. Both the voltammetry and the selective chemical dissolution hence revealed the presence of a substantial amorphous part in the samples heated at 200–400°C (see Table 1).

4. Conclusions

The thermal treatment of Ni–Mn layered double hydroxide resulted in the following three processes: (i) dehydration at 100–200°C when interlayer water was released, (ii) thermal decomposition at 220–300°C including the dehydroxylation of hydroxide layers and the decomposition of interlayer carbonate anions resulted in the formation of an amorphous mixture of oxides and (iii) crystallization of oxides—Ni2MnO8 and NiMnO3 at 400–700°C which were transformed into (Ni,Mn)3O4 spinel and NiO at 800°C and higher temperatures. Based on voltammetry measuring of the reductive dissolution reactivity, a relatively high content of amorphous part was observed in the samples heated at 200–500°C. The oxide system changed significantly at 500°C when the reactive amorphous species disappeared and the species stable up to 700°C, NiMnO3, was formed. The oxide system prepared by heating of Ni–Mn layered double hydroxide at 900–1100°C had a constant electrochemical reactivity and hence also rather stable phase composition. The results obtained by XRD, chemical analysis and voltammetry, respectively, were in a good agreement.

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