Layer Charge Sign Transition [Z]⁻ → [Z]⁺ of Lamellar Metal Oxides

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A novel topotactic process with charge sign conversion is reported for a complex layered system; the ternary oxide Na^+ $[Ni_{3/4}Fe_{1/4}O_2]^-$ with macroanion layers yields highly crystalline hydrotalcite type hydroxides $[Ni_{3/4}Fe_{1/4}(OH)_2]^{1/4+}(X^-)_{1/4}$ with macrocation layers and mobile interlayer anions *via* a redox–protolysis mechanism.
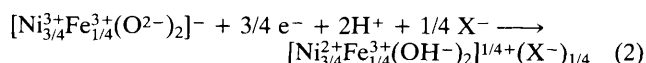
The only layered crystalline system known so far in which the layer units may behave as amphoteric species at ambient temperature is graphite which is able to form intercalation compounds $A^+[C_n]^-$ as well as $X^-[C_n]^+$.[1] Herein we report the first example of a system with complex layer units, where a change in the sign of the layer excess charge $[Z]^- \rightarrow [Z]^+$ can be observed in the course of a topotactic reaction (Z = layer unit).

It is well known that ternary oxides and chalcogenides $A^+_x[MX_2]^{x-}$ (A = alkali metal, M = transition metal, X = O,S,Se) with CdI_2 type structure undergo redox and cation exchange reactions in electrolytes.[2,3] We have investigated the reactivity of the mixed metal compound Na^+ $[Ni_{3/4}Fe_{1/4}O_2]^-$ which was prepared by reaction of the metal oxides in stoicheiometric ratio, at 750—850 °C in a dry oxygen atmosphere. The black, crystalline product (I) was monophasic, with hexagonal lattice parameters, $a = 2.97$ and $c = 15.85$ Å close to those reported for $NaNiO_2$.[4] The occupation of the octahedral intralayer positions by Ni and Fe is statistical, since no lines indicating a superstructure could be detected. Oxidimetric analysis confirmed that both transition metal ions are trivalent, *i.e.* $Na^+[Ni_{3/4}^{3+}Fe_{1/4}^{3+}O_2^{2-}]^-$. After hydrolysis and reduction with excess aqueous urea solution (pH = 12) and 0.5 M aqueous Na_2SO_3 (pH = 3—4) in air at 300 K and subsequent addition of Na_2CO_3, a new brown phase (II) is obtained with hexagonal lattice parameters $a = 3.10$ and $c = 23.46$ Å. Scanning electron microscopy showed the presence of hexagonal platelets *ca.* 4 μm in diameter and 1—2 μm in height, identical in morphology and size with those observed in the starting phase (I) except for defects typical of swelling processes in layered intercalation systems. From analytical data we assigned the composition $[Ni_{3/4}Fe_{1/4}(OH)_2(CO_3)_{1/8}$-$(H_2O)_n$, with $n = 0.7$ at ambient water vapour pressure. The compound was found to undergo anion exchange easily in aqueous solutions of pH = 3—5 according to the general scheme described in equation (1) where X_A^- and X_B^- are inorganic or organic anions. Interlayer spacings measured for a series of simple anions are given in Table 1. The selectivity sequence is $CO_3^{2-} > SO_4^{2-} > Cl^- > CH_3SO_3^- > NO_3^- > ClO_4^-$, which explains the easy formation of the carbonate form on working in air at pH >6.

$$[Z]^{1/4+}(X_A^-)_{1/4} + 1/4\ X_B^- \rightleftharpoons [Z]^{1/4+}(X_B^-)_{1/4} + 1/4\ X_A^-,$$
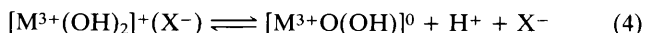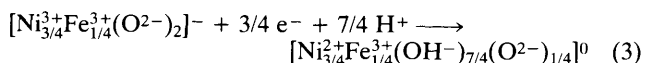$$\{Z = [Ni_{3/4}Fe_{1/4}(OH)_2]\} \quad (1)$$
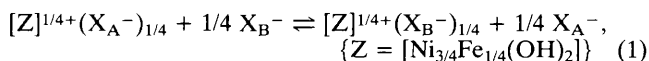
Stoicheiometry, X-ray data, interlayer spacing, chemical reactivity and co-operative exchange phenomena of these phases were found to agree well with those for transition metal hydrotalcite type phases $[M_{1-x}^{II}M_x^{III}(OH)_2]^{x+}(X^-)_x(H_2O)_n$ reported by us recently.[5] The latter compounds were obtained, however, by precipitation from homogeneous aqueous medium and exhibit small particle size and strong X-ray line broadening. The phases described here are formed in a topotactic reaction from a thermal phase and are characterized by a relatively large crystal size and the narrow line width of their X-ray reflections.

The layer charge sign conversion from macrocation to macroanion can be explained in terms of a combined redox–protolysis mechanism. Results of oxidimetric titrations were consistent with a selective and quantitative reduction of Ni^{3+} to Ni^{2+} and a conservation of the oxidation state of Fe^{3+}. The stoicheiometry of the interlayer anions and the anion exchange capacity are in agreement with these data. Simultaneously with the reduction of (I) the layer oxygen anions O^{2-} are quantitatively protonated to form OH^- groups. This step leads to a positive layer excess charge and the necessity to balance this charge with mobile hydrated interlayer anions X^-, as shown in equation (2). The surprising aspect of this reaction is that the system does not profit from the possible alternative process of a partial protonation of O^{2-} and the formation of neutral layers [equation (3)].

$$[Ni_{3/4}^{3+}Fe_{1/4}^{3+}(O^{2-})_2]^- + 3/4\ e^- + 2H^+ + 1/4\ X^- \longrightarrow$$
$$[Ni_{3/4}^{2+}Fe_{1/4}^{3+}(OH^-)_2]^{1/4+}(X^-)_{1/4} \quad (2)$$

This has to be explained in terms of the protolysis equilibrium [equation (4)]. At low concentrations of M^{3+} in the layers, the acidity of the lattice OH groups remains low and the equilibrium is on the left side in equation (4). At high concentrations of M^{3+}, partial deprotonation with formation of neutral layer units is preferred, easily demonstrated by the existence of the well known oxide hydroxides, *e.g.* $NiO(OH)$ and $CoO(OH)$, which have no layer excess charge and do not behave as anion exchangers.

$$[Ni_{3/4}^{3+}Fe_{1/4}^{3+}(O^{2-})_2]^- + 3/4\ e^- + 7/4\ H^+ \longrightarrow$$
$$[Ni_{3/4}^{2+}Fe_{1/4}^{3+}(OH^-)_{7/4}(O^{2-})_{1/4}]^0 \quad (3)$$

$$[M^{3+}(OH)_2]^+(X^-) \rightleftharpoons [M^{3+}O(OH)]^0 + H^+ + X^- \quad (4)$$

In fact, the system described here is even more complex. With weak reducing agents (*e.g.* urea–H_2O) (I) transforms first into a black intermediate carbonate phase (III) (hexagonal, $a = 3.09$, $c = 23.19$ Å), with structure and properties very similar to (II). However, the degree of oxidation of (III) is 10% higher than (II), *i.e.* a limited amount of Ni^{3+} ions are present. Phase (III) can be converted to (II) by reaction with SO_3^{2-}/H_2O. Further reduction of (II) with low potential reducing agents (*e.g.* $S_2O_4^{2-}$) in a reversible reaction finally leads to a hydrated green insulator phase (IV) with bivalent metal ions and *neutral* layer units $\{[Ni_{3/4}Fe_{1/4}(OH)_2](H_2O)_n$, hexagonal, $a = 3.11$, $c = 24.0$ Å).

Table 1. Interlayer spacing $d = c/3$ for layered hydroxides $[Ni_{3/4}$-$Fe_{1/4}(OH)_2]^{1/4+}(X^-)_{1/4}$ with mobile hydrated interlayer anions X^{n-} (measured in equilibrium electrolyte containing the corresponding anion).

X^{n-}	$d/Å$	X^{n-}	$d/Å$
CO_3^{2-}	7.82	$CH_3SO_3^-$	13.21
SO_4^{2-}	11.01	NO_3^-	10.71
Cl^-	7.96	ClO_4^-	11.86

The reactions discussed above demonstrate that the redox–protolysis transition of layered alkali–transition metal oxides represents a new method for the synthesis of hydrotalcite type lamellar hydroxides, also of interest in light of the recent use of these compounds as catalyst precursors.[6]

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