

Short communication

Nanocomposites of α -hydroxides of nickel and cobalt by delamination and co-stacking: Enhanced stability of α -motifs in alkaline medium and electrochemical behaviour

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Abstract

Dodecylsulfate-intercalated α -hydroxides of nickel and cobalt delaminate to give colloidal dispersions in 1-butanol. When these colloidal dispersions are mixed in different proportions and evaporated, composites are obtained and these consist of a random stacking of layers from the two hydroxides. The surfactant anion of these composites can be exchanged with nitrate ions and the resultant nitrate-intercalated composites are very stable in alkaline medium and show a high reversible charge capacity.

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1. Introduction

The extensive use of rechargeable batteries in electronic devices has intensified research on the design and synthesis of materials with enhanced electrochemical properties [1–3]. The hydroxide of Ni, which crystallizes as layered structures in two different polymorphic modifications, namely β and α -nickel hydroxide [4,5], is widely employed as an electrode material in alkaline rechargeable batteries [6–9]. β -Nickel hydroxide is a stoichiometric compound with the formula $\text{Ni}(\text{OH})_2$ and is isostructural with the mineral brucite, $\text{Mg}(\text{OH})_2$ while the α -form is hydroxyl-deficient and consists of positively charged layers of composition $[\text{Ni}(\text{OH})_{2-x}(\text{H}_2\text{O})_x]^{x+}$, which intercalate anions in the interlayer region to restore charge neutrality [4,5].

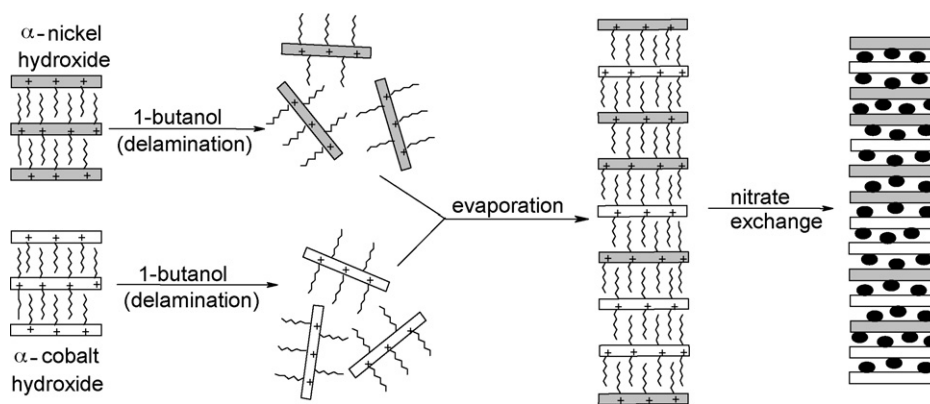
When β - $\text{Ni}(\text{OH})_2$ is employed in an alkaline battery, the electrochemical cycle involves the β - β couple in which the cycling is between β - $\text{Ni}(\text{OH})_2$ and the oxyhydroxide, β - NiOOH [10]. The overcharging of nickel hydroxide has to be avoided as it leads to an increase in the oxidation state of nickel and the for-

mation of the γ -nickel oxyhydroxide phase. The γ -phase has a higher interlayer spacing, which leads to extensive swelling and subsequent breakdown of the electrode [10]. On the other hand, the α -hydroxide and γ -oxyhydroxide phases have comparable interlayer spacings. Thus, the oxidation of α -nickel hydroxide leads to γ -oxyhydroxide without any mechanical failure [10].

Extensive studies have been carried out to achieve stabilization of the α - γ couple as an important step towards improving the capacity of nickel hydroxide based alkaline cells. This has been a challenge, however, due to the inherent instability of α -nickel hydroxide in alkaline medium where it ages rapidly to the β form [11–13]. α -Phase stabilization in alkaline medium has been achieved by partial isomorphous substitution of Ni by other metal ions, which results in the formation of layered double hydroxides (LDHs), that have been shown to exhibit stable reversible capacity [14–18].

The conversion of α -nickel hydroxide to β -nickel hydroxide is a topotactic process [11–13]. Hence, it should be possible to arrest this reaction if the layers of α -nickel hydroxide are interspersed with layers from a structurally similar layered solid. α -Cobalt hydroxide presents itself as a suitable candidate for this purpose. α -Cobalt hydroxide is isostructural with α -nickel hydroxide and though it is converted slowly into Co_3O_4 in

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Scheme 1. Schematic representation of processes involved in making nitrate-intercalated α -hydroxide composites.

alkaline medium, it is expected that this conversion too will be arrested by interspersions of the α -nickel hydroxide layers. In addition, cobalt and its hydroxides are used as additives in nickel hydroxide electrodes to improve their conductivity. Therefore, it would be interesting to synthesize and study the stability behaviour of composite solids made of the random stacking of layers of α -cobalt hydroxide and α -nickel hydroxide—a one-dimensional solid solution of the layers of the two hydroxides. Such composites could be prepared through delamination of the individual hydroxides in suitable solvents and co-stacking the layers from the colloidal dispersions so obtained. We have earlier demonstrated the delamination of surfactant-intercalated α -hydroxides [19] and the use of a colloidal dispersion of a related layered solid, a layered double hydroxide, in the preparation of nanocomposites [20].

This study concerns the synthesis of composites of dodecylsulfate (DS)-intercalated α -nickel hydroxide and α -cobalt hydroxide through delamination and co-stacking in 1-butanol, and the subsequent anion exchange of the surfactant ions of the composite with nitrate (see Scheme 1). The stability in alkaline medium and the electrochemical behaviour of the nitrate-intercalated composites are investigated.

2. Experimental

Surfactant-intercalated α -divalent metal hydroxides were prepared as described in earlier work [19]. Thirty five millilitres of a solution containing metal acetate, $M(\text{OAc})_2$ [$M = \text{Ni}$ or Co], and the surfactant (sodium dodecylsulfate) in the mole ratio 1:0.9 was added to 50 ml of 0.5 M NH_3 solution with constant stirring. The solid product was immediately centrifuged, washed free of anions with water and then with acetone, and finally dried in air at room temperature. Colloidal dispersions of surfactant-intercalated α -nickel hydroxide and α -cobalt hydroxide were prepared separately by sonicating 100 mg of the sample in 400 ml of 1-butanol at 80 °C for 1 h. Then, the two colloids were mixed (in different mole ratios, i.e., Ni:Co = 1:1, 2:1, 3:1) and sonicated for another hour. The volume of the colloidal dispersion was reduced in each case to one-tenth of its initial volume by rotary evaporation, and the resultant mixture was slowly evaporated at 65 °C in an air-oven until the solvent was completely removed.

Two-hundred milligrams each of the DS-intercalated composites (Ni–Co–DS) was stirred at room temperature in a sealed vessel for 15 days in 50 ml of ethanol in which 662 mg of KNO_3 (20 times excess of anion exchange capacity) was dispersed. After every 24 h, the supernatant was decanted and replaced by the same amount of KNO_3 dispersed in ethanol. The samples were then washed 8–10 times with water to remove excess nitrate, and 5 times with acetone to remove the adsorbed surfactant. The resultant nitrate-exchanged samples (Ni–Co– NO_3) were then dried in air at 65 °C to constant weight.

To ascertain the stability of the composites in alkaline medium, 50 mg each of the Ni–Co– NO_3 composites was stirred in 20 ml of NaOH in a sealed vessel at room temperature for 30 days. In another experiment, 50 mg each of the Ni–Co– NO_3 composites was subjected to hydrothermal treatment at pH 10 in a Teflon-lined autoclave. The solids obtained after ageing/hydrothermal treatment were washed with water until the pH of the washings reached ~ 7 , and then with acetone. The resulting solids were dried in air at 65 °C.

All the samples were characterized by powder X-ray diffraction (Philips X'Pert Pro fitted with a secondary graphite monochromator, Cu $\text{K}\alpha$ radiation, 2θ step = 2° per minute) and infrared spectroscopy (IR; Nicolet Model Impact 400D FT-IR spectrometer, KBr pellets, 4 cm^{-1} resolution). The DS-composites and the nitrate-exchanged composites were also characterized by transmission electron microscopy using a Tecnai F30 field emission microscope operated at 300 kV.

Each of the Ni–Co– NO_3 composites, graphite powder and PTFE suspension (33% suspension) in the ratio of 60:30:10 were thoroughly ground to a paste-like consistency. This paste was pressed on to a nickel foam (2.9 $\text{cm} \times 2.3 \text{ cm}$) at 120 kg cm^{-2} pressure at room temperature. The electrodes were soaked in 6 M KOH for 24 h and galvanostatically charged to 200% overcharge of theoretical capacity. All capacities are normalized to the nickel content of the active material (estimated by wet chemical analysis). The theoretical capacity for the high-performance α - γ couple is 775 mAh g^{-1} , which corresponds to an exchange of 1.7 electrons. Nickel plate counters were used for cycling and all potentials were measured against a $\text{Hg}/\text{HgO}/\text{OH}^-$ (6 M KOH) reference electrode by means of a high-impedance voltmeter. The electrodes were discharged with a constant current to a cut-off voltage of 0 V at ambient temperature (28–30 °C).

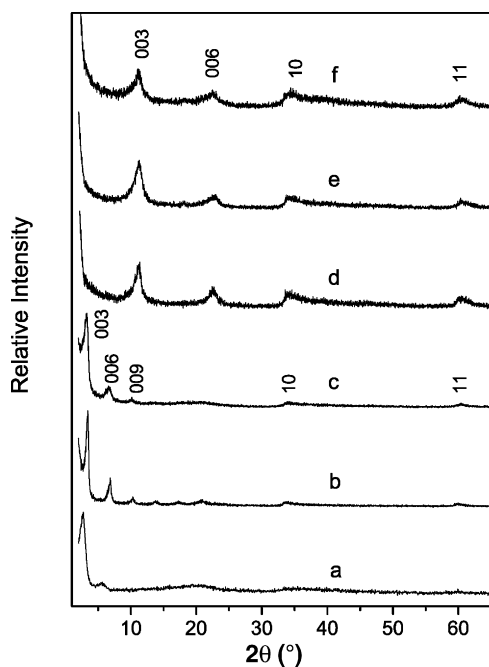


Fig. 1. PXRD patterns of dodecylsulfate (DS)-intercalated α -hydroxides of (a) Ni and (b) Co, (c) DS-intercalated composite [mole ratio = 1:1] obtained by evaporation of a mixture of colloidal dispersions of DS-intercalated α -hydroxides of Ni and Co, and (d) to (f) nitrate-intercalated composites [Ni-Co-NO₃] with Ni:Co = 1:1, 2:1 and 3:1, respectively.

3. Results and discussion

Fig. 1(a) and (b) are the powder X-ray diffraction (PXRD) patterns of the DS-intercalated α -nickel hydroxide and α -cobalt hydroxide with basal spacings of ~ 31 and ~ 26 Å, respectively. Fig. 1(c) is the PXRD pattern of the DS-intercalated composite of the α -hydroxides of nickel and cobalt (mole ratio 1:1) obtained through co-stacking. The interlayer spacing of 26.5 Å suggests that the surfactant anion is still intercalated. The small variations in the basal spacings of these samples may be due to different extents of interdigitation of the alkyl chains of the surfactant ions. Fig. 1(d) is the PXRD pattern of the Ni-Co-NO₃ composite (1:1 mole ratio) obtained through anion exchange of the DS-intercalated composite. No β -phase related reflections are seen and the basal spacing (7.9 Å) matches well with that reported in the literature for nitrate-intercalated α -nickel hydroxide [4,5]. This, in itself, is interesting as α -nickel hydroxide does not exhibit an anion-exchange reaction and any attempt to affect anion exchange results in the formation of β -nickel hydroxide. All these samples show the characteristic, saw-tooth shaped, broad peaks due to the 2D (1 0) and (1 1) reflections arising from turbostratic disorder [21,22]. Fig. 1(e) and (f) are the PXRD patterns of the nitrate-exchanged composites with mole ratios of 2:1 and 3:1, respectively. In these cases, too, β -hydroxide formation is not observed and the structure is primarily nitrate-intercalated α -hydroxide.

The IR spectrum of the 1:1 composite of DS-intercalated α -hydroxides of Ni and Co is shown in Fig. 2(a). Strong and broad absorptions are present due to hydrogen-bonded hydroxyl groups at 3500 cm⁻¹ C–H stretching vibrations of the alkyl

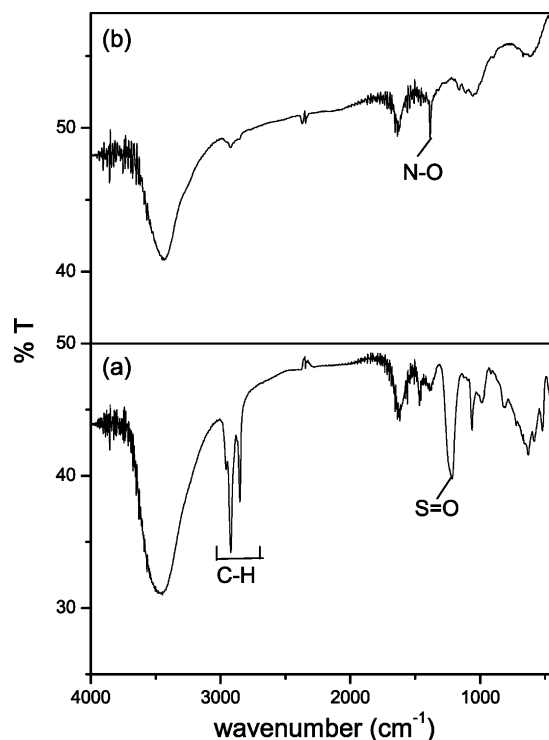


Fig. 2. IR spectra of (a) as-prepared DS-intercalated composite [mole ratio = 1:1] obtained by evaporation of a mixture of colloidal dispersions of DS intercalated α -hydroxides of Ni and Co and (b) the nitrate-exchanged α -hydroxide composite [mole ratio = 1:1].

chains of the surfactant at 2850–2950 cm⁻¹, and S=O stretching vibrations of the sulfate group at 1200 cm⁻¹. In the anion-exchanged sample (Fig. 2(b)), the presence of the N–O stretching band of nitrate ion at 1380 cm⁻¹ clearly indicates that the surfactant ions of the α -hydroxide composite have been exchanged for nitrate ions. The absence of the absorption due to S=O stretching vibration indicates quantitative replacement of the surfactant ions by nitrate ions.

In order to ascertain the stability of the composites in alkaline medium, the nitrate-intercalated composites were subjected to ageing in 1 M NaOH for 30 days and to hydrothermal treatment at 120 °C for 24 h in two separate experiments. Fig. 3(b) and (c) are the PXRD patterns of the alkali-aged and hydrothermally treated Ni-Co-NO₃ composite (1:1 mole ratio) respectively. Though these show weak reflections due to the β -hydroxide phase and the spinel Co₃O₄ phase, which arise from the partial conversion of the α -hydroxide motifs of Ni and Co to β -Ni(OH)₂ and Co₃O₄, respectively, most of the α -structure is still intact as confirmed from the strong reflection at 7.9 Å. The high stability of the composite proves that it is a random stacking of positively charged [Ni(OH)_{2-x}(H₂O)_x]^{x+} and [Co(OH)_{2-y}(H₂O)_y]^{y+} layers with charge-compensating nitrate ions in the interlayer region. Unless a few nickel hydroxide layers are placed successively, it will not be possible to form β -nickel hydroxide, and unless the cobalt hydroxide layers are adjacent to each other it will not be possible to form Co₃O₄. The composite, which is a random stacking of the two kinds of layers, has fewer regions where the like layers are continuous and

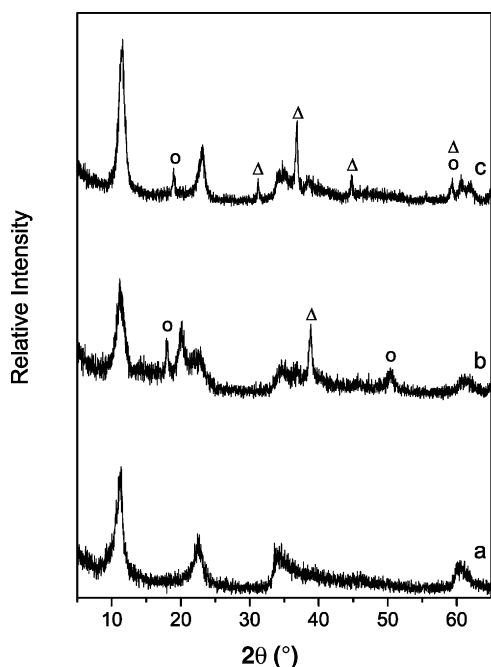


Fig. 3. PXRD patterns of (a) as-prepared nitrate-intercalated composite [mole ratio = 1:1], (b) the above sample aged in 1N NaOH for 30 days and (c) hydrothermally treated at pH 10 for 24 h at 120 °C. (○) Peaks due to β -phase, (Δ) peaks due to Co_3O_4 .

these regions convert into either β -hydroxide or Co_3O_4 , while in most of the regions the unlike neighbouring layers protect each other from such conversions.

A transmission electron micrograph of the DS-intercalated composite – mole ratio 1:1 – (Fig. 4(a)) shows large regions where fringes due to stacked layers can be observed. The spacing between the layers ($\sim 29 \text{ \AA}$) matches well with the basal spacing observed in PXRD (Fig. 1(c)). XEDS analysis of a large number of regions where the solid has fallen face flat with the c -axis perpendicular to the grid shows a constant Ni–Co ratio at all the locations and confirms random co-stacking of layers of the α -hydroxides of Ni and Co. A TEM image of the nitrate-exchanged composite (Fig. 4(b)) exhibits fringes with a spacing of $\sim 6.9 \text{ \AA}$.

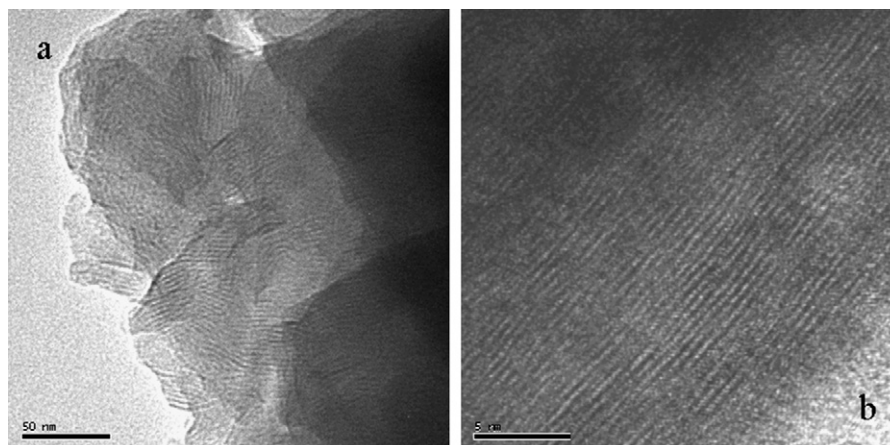


Fig. 4. TEM images of (a) DS-intercalated composite [mole ratio = 1:1] obtained by evaporation of a mixture of colloidal dispersions of DS-intercalated α -hydroxides of Ni and Co and (b) nitrate-intercalated composite obtained by anion exchange of the above sample showing lattice fringes.

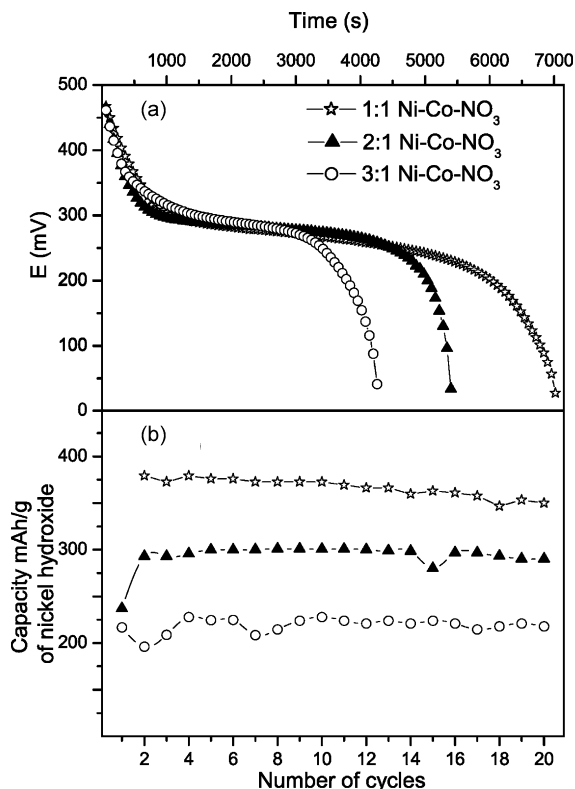


Fig. 5. (a) Galvanostatic discharge curves and (b) cycle-life data of electrodes made from composites of different mole ratios of α -hydroxides of Ni and Co-nitrate.

This is due to the fact that the sample loses the interlayer water under the electron beam, which leads to a decrease in the basal spacing.

The galvanostatic discharge curves and cycle-life data of an electrode made from different mole ratio composites Ni–Co– NO_3 are shown in Fig. 5(a) and (b), respectively. The reversible discharge capacity of the nitrate-intercalated hydroxide composite of 1:1 mole ratio in the first 10 cycles is 373 mAh g^{-1} of α -nickel hydroxide, which is equivalent to 1.89 e exchange per Ni atom. On further cycling, the

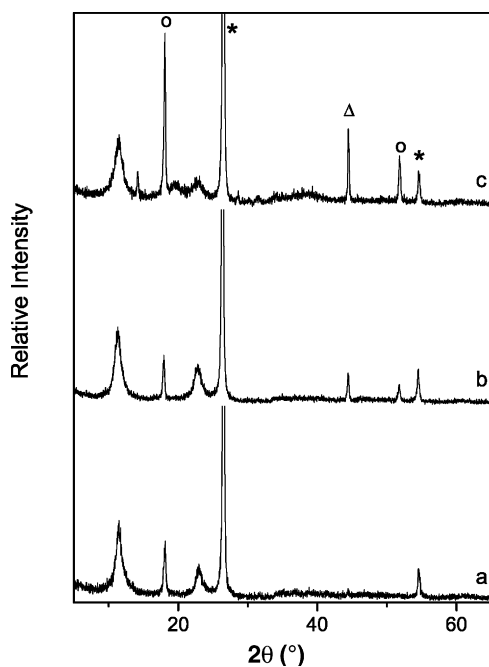


Fig. 6. PXRD patterns of composite electrodes in the discharged state after 20 cycles (a): 1:1, (b): 2:1 and (c) 3:1 composite. (○) Peaks due to β -phase, (△) peaks due to Co_3O_4 and (*) peaks due to graphite.

capacity slowly fades and after ~ 20 cycles reaches a value of 340 mAh g^{-1} of α -nickel hydroxide, equivalent to 1.7 e exchange per Ni atom and corresponding to 100% active material utilization [23]. The PXRD pattern of the discharged electrode (Fig. 6(a)) after 20 cycles indicates the continued existence of the α -phase. The initial higher capacity of the electrode may be attributed to the formation of conductive CoOOH during the charging process, while the decrease in capacity over a large number of cycles is possibly due to the reduction of Co^{3+} to Co^{2+} , as suggested by Faure et al. [17].

The 2:1 and 3:1 Ni–Co– NO_3 composites deliver constant reversible discharge capacities of 300 and 204 mAh g^{-1} of α -nickel hydroxide, respectively, over 20 cycles. The capacities of the composites decrease linearly with decrease in α -cobalt hydroxide content. This is expected as the stability of the composite in an alkaline medium will decrease with α -cobalt hydroxide motif content. With decrease in α -cobalt hydroxide content, the composite will have more regions where α -nickel hydroxide motifs are continuously stacked and lead to facile conversion into β -phase. This is indicated by the PXRD patterns of electrodes made of the different composites after 20 cycles, as shown in Fig. 6. In the case of the electrode made of 1:1 composite, the (001) reflection of the β -phase is observed and reflections due to Co_3O_4 are almost absent. For the 2:1 composite, in addition to the β -phase related reflections there are reflections due to Co_3O_4 . The intensities of the reflections due to these phases are further increased for the 3:1 composite.

4. Conclusions

A layered, one-dimensional, solid solution of α -hydroxides of Ni and Co has been prepared, in which the layers from the parent hydroxides are randomly co-stacked. This co-stacking arrests the ageing reactions of both the hydroxides in alkaline medium and results in stabilization of the α -phase. The composites show high reversible discharge capacities for alkaline battery applications due to the enhanced stability of the α -structure.

Acknowledgements

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