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Short communication

Nickel hydroxide, a reverend classic for rechargable batteries—Comment on an article on NiO electrodes for supercapacitors, this journal 74 (2016) 241–247

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ABSTRACT

A reappraisal of a recently published experimental study of a new positive electrode material for supercapacitors [this journal 74 (2016) 241–247] is presented. It is concluded that a comparison with already available technology should always come first when evaluating the performance of a new electrode material. In this context, the long history and undiminished practical importance of nickel hydroxide as a positive electrode material are noted. The relevance of basic college chemistry for experimental work on new electrode materials is demonstrated. The desirability of providing reliable literature references in connection with such work is emphasized.

1. Introduction

In a recent article, Wen at al. [1] describe the synthesis and characterization of nanoscale nickel oxide, NiO, both supported on carbon nanotubes, CNTs, and unsupported, and present data on its performance as a supercapacitor electrode material. The NiO is reported to have been prepared hydrothermally by homogeneous precipitation from a dilute aqueous solution containing nickel nitrate and urea at 110 °C in an autoclave within three hours. From freshman chemistry one recalls that hydroxides of basic cations like Ni^{2+}, in contrast to more acidic, amphoteric ones like Cu^{2+} or Zn^{2+}, are not prone to thermal dehydration to the respective oxides upon precipitation from aqueous solution. NiO should not, therefore, have been formed from the precipitated $Ni(OH)_2$ under the conditions given above. Indeed, the x-ray powder diffractogram of the CNT-supported material (Fig. 2(a) [1]) appears to fit turbostratically disordered $Ni(OH)_2$ rather than NiO. As the basic assumption on which the article [1] is based is thus from the outset called into question, a reappraisal of the results seems to be called for.

2. Hydrothermal synthesis of nickel hydroxide

As mentioned in the introduction, $Ni(OH)_2$ is not expected to dehydrate to NiO under hydrothermal conditions. Yet, in the experimental section of the cited article [1] it is stated that NiO was obtained by homogeneous precipitation from a $Ni(NO_3)_2$-solution containing urea as an ammonium carbonate precursor at 110 °C in an autoclave within three hours. The diffractogram of the CNT-supported sample (Fig. 2(a) [1]) does not bear out this statement as it appears to match turbostratically disordered $Ni(OH)_2$ rather than NiO (see Section 3 below). The diffractogram, shown in the same figure, of the unsupported sample, however, does indeed correspond to nanoscale NiO. Such a result is at odds with virtually all previously published work that we are aware of, a fact not commented upon in the article [1]. A subsequent annealing step which would lead to NiO is, in fact, indicated in Scheme 1 [1] but neither referred to in the experimental section nor explained in the remainder of the article [1]. Adding to the confusion, the x-ray powder pattern of NiO is incorrectly indexed in the main text of the article [1], a 001 reflection at $2\theta = 10.2°$ being referred to even though that would be extinguished in the fcc structure and, indeed, is absent from the powder pattern (Fig. 2(a) [1]). In fact, this 001 reflection is only expected for $Ni(OH)_2$. Regarding the impossibility of obtaining NiO hydrothermally even at temperatures of up to 350 °C the following references – covering five decades and including one reference from this journal [2] – may be consulted among many others: (i) Under very similar conditions to those given in the article [1], but with added surfactant, only turbostratic hydrous $Ni(OH)_2$ is obtained from a $Ni(NO_3)_2$/urea solution maintained at 120 °C for 24 h [3]; (ii) graphene or graphene-oxide-supported hydrous $Ni(OH)_2$ recrystallizes upon hydrothermal treatment at 180 °C yielding β-$Ni(OH)_2$ but no NiO [4];

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(iii) similarly, unsupported hydrous $Ni(OH)_2$ yields β-$Ni(OH)_2$ hydrothermally after 24 h [5] or 48 h [6] at 180 °C, after 5 h at 200 °C [7], after 24 h at 250 °C [8], after 20 h at 270 °C [9] or after 6 h even at 350 °C [2]. Urea has been used repeatedly in recent years to hydrothermally precipitate turbostratic $Ni(OH)_2$ – but not NiO – from homogeneous solution, e.g. at 80 °C [10,11] or 90 °C [12]. In order to dehydrate $Ni(OH)_2$ to the oxide, NiO, it must be heated to at least 200 °C under sufficiently low water partial pressure, as is clear from previous reports in this journal [13] and elsewhere [14,15]. From thermogravimetric analysis (TGA) and differential thermoanalysis (DTA) it is well known that an endothermic loss of water takes place at about 280–340 °C depending on measurement conditions like heating rate or gas flow rate. Thus, in many publications from the past decades approximate values may be found of the temperature at which the endothermic weight loss peak occurs, e.g. 281 °C [16], 285 °C [17], 290 °C [3], 280–310 °C [18], 320 °C [11], 326 °C [7] and 340 °C [19]. According to the TGA measurement reported in the cited article (Fig. 2(b) [1]), the CNT-supported material features a weight loss of about 20% at approximately 320 °C. This, together with a continued weight loss at increasing temperatures, is interpreted in the article [1] as an oxidative destruction of the CNTs. A literature citation is provided in support of this assumption but such a result does not seem to have been discussed in the cited publication (reference 41 in the article [1] – further instances of misquoted references will be given in the conclusion, Section 5). It appears, therefore, that the weight loss is due to the dehydration of the CNT-supported $Ni(OH)_2$ – whereby NiO is formed – rather than to an oxidation of the CNTs. This is in accord with the previously reported decomposition temperatures quoted above as well as with the theoretical weight loss of $Ni(OH)_2$ of 19.4%. The CNT-content would have been less than 10% judging from the amount employed in the synthesis and thus makes little difference here as long as the CNTs are not oxidized. Only the continued weight loss above 320 °C may indeed have been due to an oxidation of the CNTs especially since the NiO already formed is a potent oxidation catalyst for organic substrates.

3. Structure of nickel hydroxide

Way back in 1925, the crystal structure of brucite-type $Ni(OH)_2$ – called β-$Ni(OH)_2$ today – was elucidated from Debye-Scherrer photographs by Giulio Natta [20,21]. Soon after, in 1936, frequent turbostratic disorder in this layered hydroxide, sometimes even accompanied by variable interlayer spacing due to irregularly intercalated water or foreign ions, was recognized by Lotmar and Feitknecht [22]. Such partially disordered polymorphs are called α-$Ni(OH)_2$ today. Even in 1932, the mathematical formalism for a description of the rather unsymmetrical and broad hk-reflections of turbostratic structures (two-dimensional nets in general) had been introduced by Max v. Laue [23]. Thus, by the 1940ies, the cause of the characteristically unsymmetrical and broad shape of the reflections had become common knowledge in x-ray powder diffraction [24]. Over the last half-century, innumerable articles have been published on the structure, (electro-) chemistry and magnetism of $Ni(OH)_2$, not least due to its continuing preeminence as a positive electrode material in low-cost rechargable batteries (see Section 4 below). It is not hard, therefore, to find examples of powder diffractograms of turbostratic α-$Ni(OH)_2$ in the literature spanning several decades [3,10–12,16,17,19,25]. Even diffractograms of α-$Ni(OH)_2$ in a highly dispersed state, supported on amorphous silica [26], and the profiles of some individual reflections [27] have been reported. Such diffractograms, although admittedly rather varied, prove on the whole to be quite similar to the one shown in the article for the CNT-supported material (Fig. 2 (a) [1]). We have reproduced the latter along with one example from the literature [19] in Fig. 1 (where each trace has been

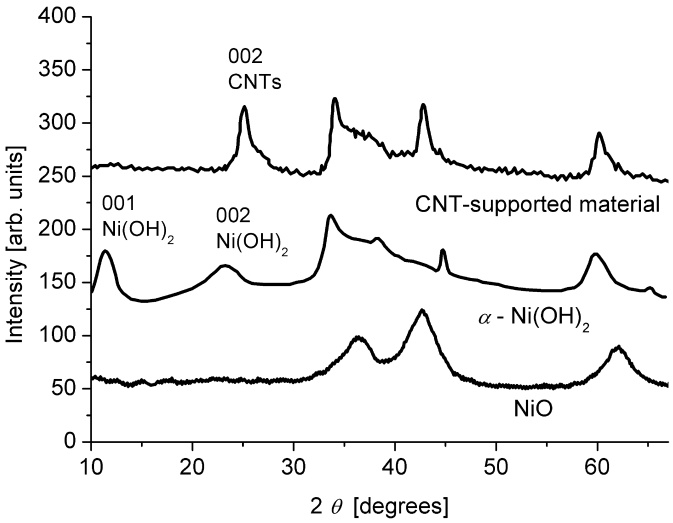

Fig. 1. X-ray powder diffractograms (Cu-K_α radiation), digitized from the cited article [1] (top and bottom) and from the literature [19] (center).

digitized point by point from the corresponding figure in the respective original publication). Apart from the additional 002 reflection of the CNTs, the missing 001/002 reflections of the turbostratic α-$Ni(OH)_2$ and a 2θ-offset of about 0.5°, the diffractogram from the article [1] (Fig. 1, top) does not differ unduly from the one previously reported for α-$Ni(OH)_2$ [19] (Fig. 1, center). The reflections in the central region (2θ = 30–50°) are known to be rather variable for turbostratic α-$Ni(OH)_2$ (compare the series of references from several decades cited above). Both the shape and the position of the reflections, however, do differ significantly from those of NiO as also digitized from the article (Fig. 2(a) [1]) and included here (Fig. 1, bottom). From a comparison of these three diffractograms it appears, therefore, that the CNT-supported material, the primary object of study in the article [1], was turbostratic α-$Ni(OH)_2$ rather than NiO. The fact that the 001 and 002 reflections are absent – comparable to the case of silica-supported $Ni(OH)_2$ [26] – may be due to irregular intercalation of interlayer species as noted by Lotmar and Feitknecht [22]. Alternatively, because of the widened interlayer spacing, the strong 001 reflection may have been shifted to 2θ angles below 10° (Cu-K_α radiation) [16,27], a region not shown in the article (Fig. 2 (a) [1]). More boldly, one might speculate that monolayer $Ni(OH)_2$ sheets – which cannot give rise to 001/002 reflections – had formed on the CNTs, as previously surmised in the case of silica-supported $Ni(OH)_2$ [26].

4. Performance of $Ni(OH)_2$-based battery electrodes

Nickel hydroxide was introduced as a positive electrode material for rechargable batteries simultaneously by Waldemar Jungner in Sweden and Thomas Alva Edison in the USA in 1901 [28]. Since then it has gone from strength to strength as a cheap and robust electrode material and is omnipresent in nickel-metalhydride accumulators today. Thus, we are empirically probably not less thoroughly acquainted with it than with the even older but still equally ubiquitous and irreplacable electrodes of the lead-acid-battery. Since, as a matter of fact, the cited article [1] deals primarily with $Ni(OH)_2$ rather than NiO, as shown in the preceding sections, one may inquire how the new findings compare with previous knowledge regarding $Ni(OH)_2$. Upon inspection of the cyclic voltammogram (Fig. 3(a) [1]) and the galvanostatic charge/discharge curves (Fig. 3(c) [1]) for the CNT-