

## Infrared spectroscopic studies of the oxide-hydroxides of Ni, Co and Mn

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Metal oxide-hydroxides of the general formula  $MO(OH)$  ( $M=Ni^{3+}$ ,  $Co^{3+}$  and  $Mn^{3+}$ ) are actually bronzes of the corresponding quadrivalent metal oxides and should be represented as  $H_xMO_2$  ( $x=1$ ). Infrared spectroscopic studies show that these compounds do not exhibit any hydroxyl stretch. The protons seem to be delocalized between slabs of  $MO_2$ .

Metal oxide-hydroxides of  $Ni^{3+}$ ,  $Co^{3+}$  and  $Mn^{3+}$  are known to play a major role in the charge-discharge cycle of nickel hydroxide [1], cobalt hydroxide [2,3] and manganese dioxide [4] electrodes respectively. A complete characterization of these phases is therefore essential to our understanding of the electrode reactions taking place at these oxide electrodes. In particular the nature of the hydroxyl species in the oxide-hydroxides has not been clearly understood. Melendres et al. [5], from a study of the Raman spectra of the higher oxides of nickel, have opined that the formulation of the oxide-hydroxide of nickel as  $NiO(OH)$  is incorrect. In this communication we report our infrared spectroscopic studies of the oxide-hydroxides of  $Ni^{3+}$ ,  $Co^{3+}$  and  $Mn^{3+}$  and compare the results with those of the corresponding divalent hydroxides.

All compounds studied here were prepared by the method of Brauer [6] and characterized by X-ray diffraction. The X-ray diffractograms were found to match with those reported for these compounds in the JCPDS powder diffraction file [7]. As observed by other authors [5,8], the diffraction patterns of the nickel compounds were broad, indicative of poorly ordered samples.

All infrared spectra were recorded on a Perkin-Elmer model 684 IR spectrometer with KBr pellets on CsI windows at a resolution of  $3\text{ cm}^{-1}$ .

In fig. 1 are shown the infrared spectra of  $Ni(OH)_2$  and  $NiO(OH)$ . The OH stretching region and the metal oxygen stretching region ( $800\text{--}200\text{ cm}^{-1}$ ) are both shown in detail.

$Ni(OH)_2$  shows a sharp peak at  $3630\text{ cm}^{-1}$  followed by a broad band from  $3500$  to  $3200\text{ cm}^{-1}$  indicating the presence of both free and hydrogen-bonded hydroxyl groups. Both the  $\alpha$  and  $\beta$  forms of  $Ni(OH)_2$  have varying amounts of water of hydration [8,9] and the broad band in the OH stretching region has a significant contribution from the water of hydration.  $NiO(OH)$ , on the other hand, shows only a broad weak absorption in the range  $3600\text{--}3100\text{ cm}^{-1}$  precluding the presence of free hydroxyl groups in this compound.

In the low-frequency ( $800\text{--}200\text{ cm}^{-1}$ ) region,  $Ni(OH)_2$  shows a complex spectrum with broad bands at  $525$  and  $450\text{ cm}^{-1}$  and a sharp peak at  $350\text{ cm}^{-1}$ .  $NiO(OH)$  shows a broad band at  $570\text{ cm}^{-1}$  and a shoulder at  $460\text{ cm}^{-1}$ .

In fig. 2 are shown similar results for the cobalt system.  $Co(OH)_2$  shows a sharp OH stretch at  $3620$

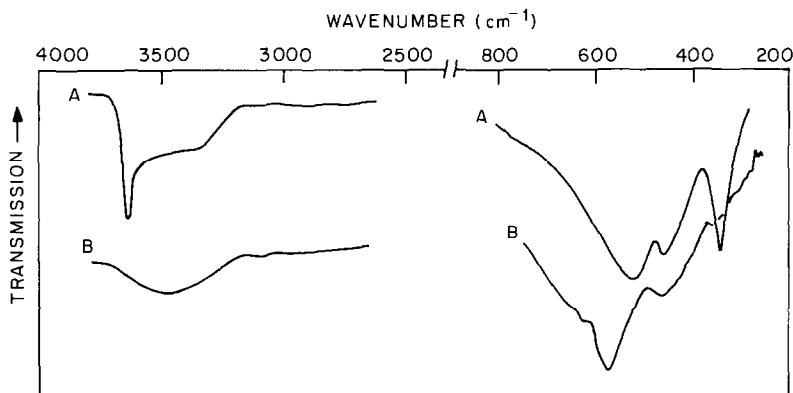


Fig. 1. Infrared spectra of  $\text{Ni}(\text{OH})_2$  (A) and  $\text{NiO}(\text{OH})$  (B).

$\text{cm}^{-1}$  followed by a broad band in the  $3500\text{--}3000$   $\text{cm}^{-1}$  region. In the low-frequency region it shows a spectrum similar to that of  $\text{Ni}(\text{OH})_2$  with bands at  $480$  and  $440$   $\text{cm}^{-1}$  and a sharp peak at  $300$   $\text{cm}^{-1}$ .  $\text{CoO}(\text{OH})$ , on the other hand, shows a weak broad absorption band in the  $3600\text{--}3100$   $\text{cm}^{-1}$  region and there is clearly no indication of the existence of any free hydroxyl group. In the low-frequency region, the spectrum of  $\text{CoO}(\text{OH})$  is very simple with a single band at  $580$   $\text{cm}^{-1}$ . There is a pronounced asymmetry on the low-frequency flank.

In fig. 3 is shown the spectrum of  $\text{MnO}(\text{OH})$ . Once again the  $3600\text{--}3000$   $\text{cm}^{-1}$  region shows no free OH stretching frequency, while the low-frequency region is very complex with bands at  $610$ ,  $490$ ,  $400$  and  $330$   $\text{cm}^{-1}$ , respectively.

Structurally well-defined hydroxides of brucite

structure exhibit a sharp peak in the OH stretching frequency region [5], indicating the presence of free hydroxyl groups. The trivalent oxide-hydroxides, which are known to form by the oxidation of the divalent hydroxides at the oxide electrodes do not show any well-defined OH stretching modes. Free hydroxyl groups are therefore absent in the oxide-hydroxides. It may therefore be more appropriate to formulate these compounds as oxides rather than oxide-hydroxides. However, the X-ray diffraction patterns as well as the infrared spectra of these trivalent phases are different from those of the well-known divalent oxides of Ni, Co and Mn, indicating that they are not the same. Melendres et al. [5], from a group theoretical analysis of their Raman spectra, have interpreted the trivalent nickel oxide-hydroxide phase as derived from the quadrivalent  $\text{NiO}_2$ . A similar

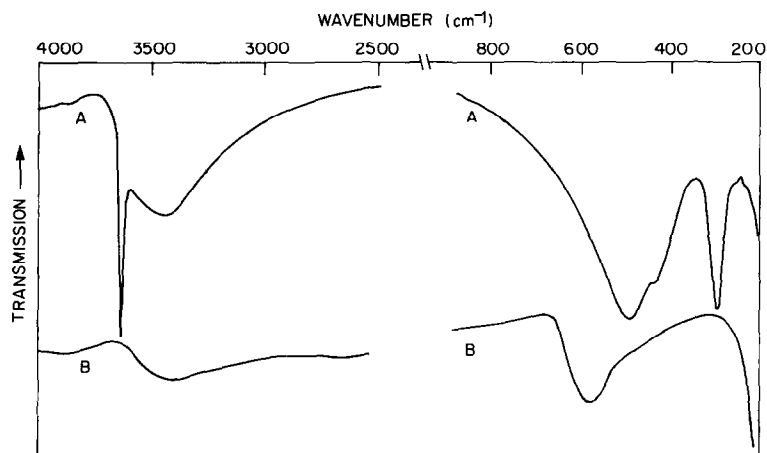


Fig. 2. Infrared spectra of  $\text{Co}(\text{OH})_2$  (A) and  $\text{CoO}(\text{OH})$  (B).

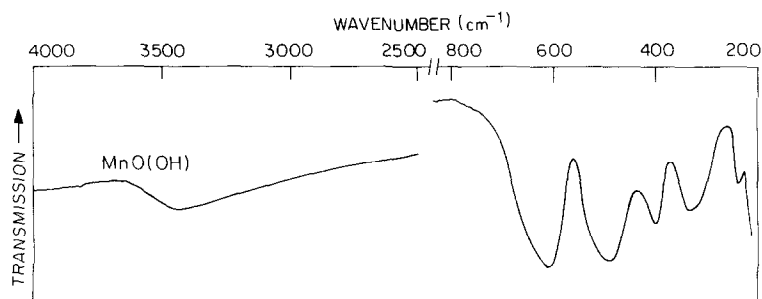


Fig. 3. Infrared spectrum of MnO(OH).

conclusion can be extended to the case of Co and Mn as well. The oxide-hydroxides can then be formulated as bronzes of the type  $H_xMO_2$  ( $x=1$ ).  $x=2$  represents end members of the series which are well-defined hydroxides of the brucite structure. Brucite structure consists of layers of  $MO_2$  with the protons sticking out into the interleaving space [10]. The OH bond axis is parallel to the  $c$  axis of the crystal. The proton layer is saturated as all the oxygens are bound to a proton each.

Oxidation appears to occur by proton extraction and when this happens vacancies are created in the proton layers, as some oxygens are no longer bound to a proton. The protons either become delocalized or get positioned at sites which are less well defined than earlier leading to the disappearance of the free hydroxyl stretching mode in these compounds and the phase acquires a bronze-like character. Fig. 4 illustrates this model pictorially. This model qualitatively explains the two observed phenomena: (1) Corrigan and Knight [11] have evaluated the charge on Ni on an oxidized nickel hydroxide electrode to

be  $3.6 \pm 0.1$ , a result compatible with the identification of the phase as  $H_xNiO_2$  ( $x=0.4$ ). Buss et al. [12] in similar work on cobalt hydroxide electrodes have achieved an oxidation state of 3.7. (2) The delocalization of the protons also explains the high proton diffusion coefficients [13] of the nickel hydroxide electrodes.

Further investigations on the oxide-hydroxides of other metals are currently in progress.

## References

- [1] P. Oliva, J. Leornarde, J.F. Laurent, C. Delmas, J.J. Braconnie, M. Figlarz, F. Fievert and A. de Guibert, *J. Power Sources* 8 (1982) 229.
- [2] R.D. Armstrong and E.A. Charles, *J. Power Sources* 25 (1989) 89.
- [3] J. Bauer, D.H. Buss, H.J. Harms and O. Glemser, *J. Electrochem. Soc.* 137 (1990) 173.
- [4] B.D. Desai, J.B. Fernandes and V.N. Kamat Dalal, *J. Power Sources* 16 (1985) 1.
- [5] C.A. Melendres, W. Paden, B. Tani and W. Walczak, *J. Electrochem. Soc.* 134 (1987) 762.
- [6] G. Brauer, *Handbook of preparative inorganic chemistry* (Academic Press, New York, 1965).
- [7] J.V. Smith, ed., *Powder diffraction file*, Joint Committee on Powder Diffraction Standards, Pennsylvania (1967).
- [8] B. Mani and J.P. de Neufville, *J. Electrochem. Soc.* 135 (1988) 800.
- [9] H. Bode, K. Dehmelt and J. Witte, *Electrochim. Acta* 11 (1966) 1079.
- [10] H. Krebs, *Fundamentals of inorganic crystal chemistry* (McGraw-Hill, New York, 1968).
- [11] D.A. Corrigan and S.L. Knight, *J. Electrochem. Soc.* 136 (1989) 613.
- [12] D.H. Buss, J. Bauer, W. Diembeck and O. Glemser, *J. Chem. Soc. Chem. Commun.* (1985) 81.
- [13] D.M. MacArthur, *J. Electrochem. Soc.* 117 (1970) 729.

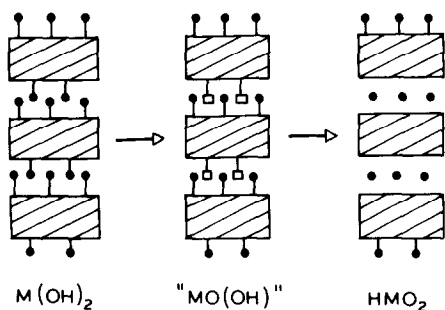


Fig. 4. Schematic model to explain the bronze-like behaviour of the oxide-hydroxides. The hatched region represents slabs of  $MO_2$ . ● represents a proton, □ represents a vacancy.