

Crystal chemistry and valence determinations for Mn, Ni and Co oxides as cathode materials in Li batteries



Elena Levi*, Doron Aurbach

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel

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ABSTRACT

Cation charge distribution is one of the basic problems for cathode materials in Li and Na batteries. This work analyzed the valence–distance relationship for a large number of Ni, Mn, and Co oxides. It uses high quality structural data obtained recently, and takes into account the influence of lattice strains on the bond lengths. The linear character of the valence–distance correlation for the Ni and Mn cations allows for an accurate valence determination from the average Mn–O and Ni–O distances in the charge range from +2 to +4. The correlation for Co is more complicated, and the unambiguous valence assignment is possible only in the range from +2 to +3. Although we used mainly the diffraction data to establish the valence–distance relationships, in many cases, especially for the mixed oxides, the assignment of Ni, Mn, and Co oxidation states should be done based on the local structure descriptions obtained by X-ray absorption spectroscopy. Important examples are presented to illustrate the use of the valence–distance correlations for detailed structural analysis, especially for the lattice strain determinations.

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1. Introduction

Mn–Co–Ni-oxides have recently gained much attention as promising candidates for high-energy cathodes in Li and Na batteries [1–3]. The oxidation state of a transition metal (TM) in such cathodes is one of the basic parameters for the material capacity and operating voltage [4,5]. It may change from +2 to +4 for Ni and from +3 to +4 for Co and Mn. A difference in the cation charges may also result in the cation ordering and order–disorder phase transitions in the crystal structure of intercalation compounds [6,7]. In addition, the issue of the TM charge is important for the problem of the electrode stability during electrochemical polarization. In general, the lower the charge of the ions, the higher is their mobility in solid hosts [8]. Thus, the presence of divalent Ni, Mn or Co ions in the intercalation compounds should decrease their structural stability. For instance, Reed et al. [9] explained a fast conversion of the layered Li_xMnO_2 to spinel-like material by the presence of Mn^{2+} cations, resulting from the charge disproportionation reaction:



According to Thackeray [10], this reaction is also responsible for Mn dissolution upon cycling and subsequent electrode degradation.

It is well known that the cation valence can be estimated from the experimental cation–anion distances by their comparison with typical (or ideal) bond lengths. The latter can be obtained as a sum of the Shannon radii [11] for oxygen and respective cation (the Shannon

radii take into account different oxidation and spin states of the cations and their coordination). The valence value can be also found as the bond valence sum, based on the experimental cation–anion distances and tabulated bond valence parameters [12]. For ionic compounds with strict cation ordering, the knowledge of the crystal structure is commonly sufficient for the atomic valence determinations. However, sometimes the local atomic structure around cations differs from the average crystal structure obtained by diffraction methods, in particular, in solid solutions, where the same crystallographic sites can be occupied by cations of different sizes. For instance, in the layered Li–Mn–Co–Ni-oxides, Ni^{2+} (Shannon ionic radius of 0.69 Å) may be substituted by Co^{3+} (0.545 Å), Mn^{4+} (0.53 Å) and even by Li^+ (0.76 Å). In such compounds the “diffraction” interatomic distances are, in fact, the average values for Ni–O, Co–O, Mn–O and Li–O bonds. In this case the valence determinations should not be based on the “diffraction” distances, but rather on those obtained by X-ray absorption spectroscopy [13] (see example in Section 5).

In spite of the common application of the valence–distance method in spectroscopic studies, the calibration curves presented by different authors for the TM oxides are not always consistent. For example, Capehart et al. [14], as well as Farley et al. [15], based on the data for a few Ni oxides and hydroxides ($\text{K}(\text{NiO}_2)_3$ or KNiO_6 , $\text{Ni}(\text{OH})_2$ and NiO), showed the linear relationship between the Ni valence and the length of the Ni–O bonds in the whole charge range between +2 and +4. In contrast, according to Takeda et al. [16] and Mansour & Melendres [17], who used the Shannon radii, the curve is not linear, and the valence–distance relations for the Ni–O bonds differ effectively in the ranges from +2 to +3 and from +3 to +4.

It is worth emphasizing that for many purposes it is sufficient to use the ionic radii obtained by Shannon in 1976 [11]. However, in our study we are interested in very delicate changes in the crystal structure

* Corresponding author.

E-mail address: elenal@mail.biu.ac.il (E. Levi).

caused by steric effects (see Sections 3 and 4). From the classic work of Pauling [18], a steric mismatch between ion sizes in the crystal structure and the influence of this mismatch on the stability of ionic compounds remains to be one of the basic problems in solid chemistry. A well-known example is the perovskite ABO_3 family, for which the tolerance factor describing the size mismatch for A and B cations serves as an indicator for stability and distortion of the crystal structures [19]. This mismatch results in the lattice strains, which, in turns, can be characterized by the deviation of the cation valences from the expected values [12,20]. For compounds with more flexible chalcogenide framework the lattice strains may reach especially high values. For instance, the bond valence sum for the large Ba^{2+} cation in $BaMo_6S_8$ was found to be equal to 3 v.u. (valence unit) as compared to the normal value of 2 v.u. obtained for such a relatively small cation as Sn^{2+} in $SnMo_6S_8$ [21]. For oxides, the changes in the chemical bonds are less pronounced. In this case it is crucial to know first of all the exact values of the unstressed chemical bonds for the cation–anion pairs (TM–O) for different oxidation states of the TM.

Thus, the main aim of this paper is to obtain proper correlations between the average TM–O distances and the TM valence (TM = Ni, Co, Mn), based on recent and more precise structural data for a large number of Mn, Co and Ni-oxides. These correlations can be used as calibration curves for accurate valence determinations in spectroscopic and structural studies. In addition, they are especially important in a fine structural analysis, in particular in the determination of the lattice strains. We also show later in the paper how the “experimental” valences can be used to estimate the lattice strains and finally to explain ordering and instability in the layered oxides (see examples in Sections 3–5).

2. Valence–distance correlations for Mn, Ni and Co cations in their oxides

Fig. 1 shows the calibration graphs relating the TM–O distances in the crystal structures of various Mn, Co and Ni-oxides to the valence of TM. Each point represents an average experimental value of the TM–O distances obtained for a given compound with the known oxidation state of TM. For some of the compounds we used high quality data obtained by different researchers and by different diffraction methods (see Tables 1–3, refs. [6,15,16,22–93]). Since in most battery materials the oxygen atoms are closely packed, we are interested only in the octahedral and tetrahedral coordinations for the TM cations. In principle, any valence value for such cations can be characterized by typical cation–anion distance. The dispersion of the average TM–O distances for different compounds in Fig. 1 from the “ideal” values is caused by limitations in the experimental accuracy (typically ~ 0.02 Å), as well as by lattice strains [12], which arise due to the steric conflicts in the atomic arrangement. Both the factors (experiment quality and strain possibility) were taken into account in the compound choice.

For comparison, Fig. 1 shows also the TM–O distances (marked in red for the octahedral coordination and in blue for the tetrahedral one) calculated as a sum of the Shannon radii for oxygen and respective TM cations. As can be seen, for Mn and Ni ions in octahedral coordination the black points obtained from the experimental data can be fitted by linear regressions ($R^2 > 0.98$ and 0.95 , respectively). It means that the valence determinations performed based on the experimental Mn–O or Ni–O distances should provide accurate results. In contrast, for the Co ions the regression is rather polynomial ($R^2 \approx 0.95$). As a result, it should be feasible to distinguish between Co^{2+} and Co^{3+} ions, but the valence assignment in the charge ranging from +3 to +4 seems to be problematic.

As can be seen from Fig. 1, the limitation of the study to close-packed oxides has some advantage: we can use the calibration curves without knowledge of the spin state of the TM cations in the compounds under study. It is necessary only to know the coordination number of the TM (6 or 4). The “experimental” valence of the TM cation can be found directly from the average value of the experimental TM–O

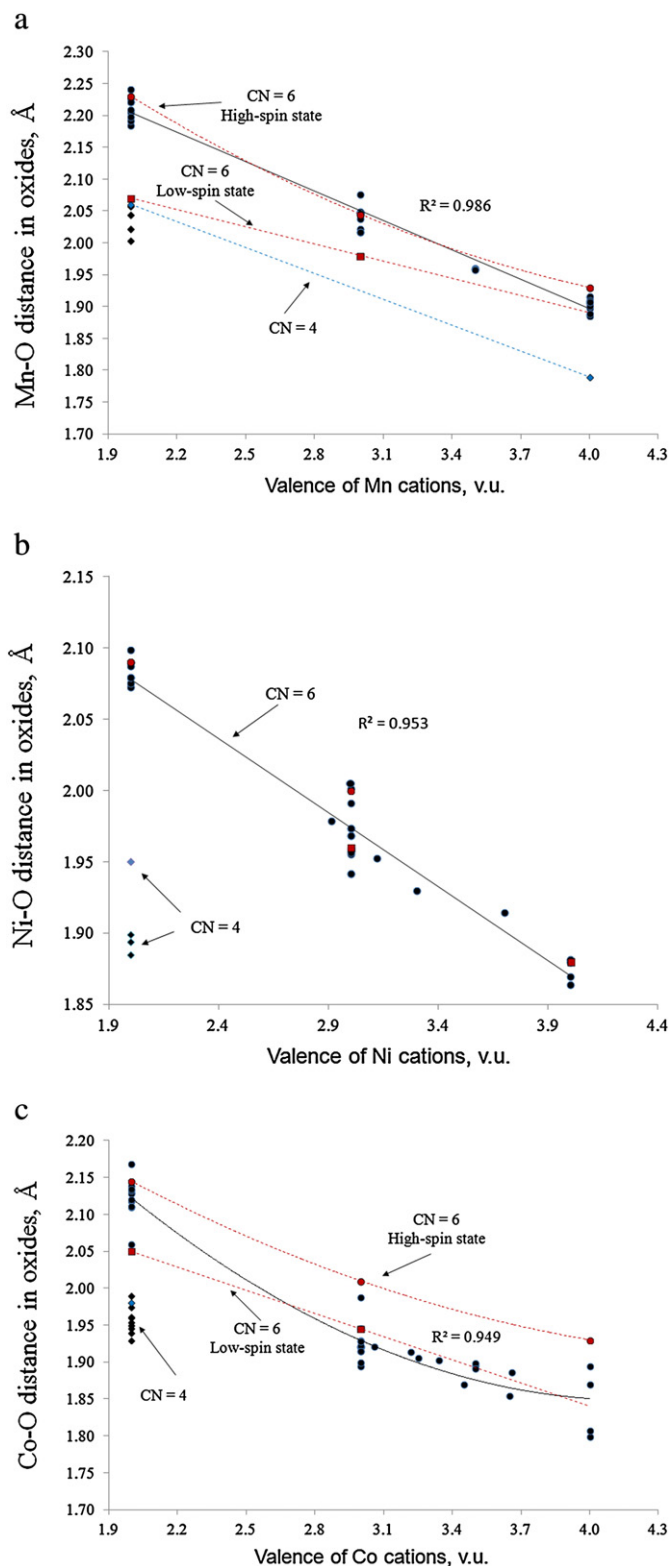


Fig. 1. Calibration graphs relating the average TM–O distances in the crystal structures of various oxides to the valence of TM: TM = Mn (a), Ni (b) and Co (c). Each black point represents a compound with the known oxidation state of TM (see Tables 1–3). The black circles and diamonds correspond to octahedral and tetrahedral coordination of TM, respectively. The red circles and squares present the sums of the Shannon radii for the TM cations in octahedral coordination, in the high and low spin states, respectively. The blue diamonds are the same sums for TM cations in tetrahedral coordination.

distances established by diffraction or spectroscopic methods. For instance, the presence of two TMs in spinel $NiFe_2O_4$ does not allow for a simple determination of the Ni oxidation state from the compound

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