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The electrochemical stability of lithium-metal oxides against metal reduction

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Abstract

The possibility of metal reduction during the charging of secondary lithium batteries with Li_xMO_2 cathodes is investigated. Loss of active material due to metal reduction can be one of the causes of capacity decay in these batteries after repeated charging. First principles methods are used to calculate the metal reduction potentials in layered Li_xMO_2 compounds where $M = \text{Ti, V, Mn, Fe, Co}$ or Ni . It is found that, for several of these compositions, the metal ions may preferably reduce before the lithium ion during charging. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Lithium batteries; Intercalation; First-principles calculation

1. Introduction

The growing desire for portable electronic devices and rechargeable power sources has fueled a strong interest in lithium batteries and the scientific and technological problems associated with them. The advantages of the Li battery concept over current battery technologies are numerous: High gravimetric and volumetric energy density, high single-cell voltage, no memory effect, and the potential to be fabricated out of all nontoxic materials. However, practical developments are limited by concerns over safety and long-term reliability [1]. Li batteries tend to lose a significant fraction of their capacity after repeated charging and discharging.

In a lithium battery, Li^+ ions are shuttled back and

forth between an anode, where Li resides at high chemical potential, and a cathode where the Li chemical potential is low, Fig. 1. The active component of a cathode is typically a lithium-metal oxide. These compounds can store a substantial amount of Li (on the cathode side) during the discharge cycle of the battery and release it again upon charging. The Li is stored by ionic insertion into the crystal structure of the host material. The capacity of the battery depends directly on this amount of Li that can be inserted and removed reversibly from the lithium-metal oxide. Because Li resides at very low chemical potential in these oxides, high single cell voltages can be obtained with lithium-metal oxide cathodes. A material such as Li_xCoO_2 intercalates Li around 4V against a metallic Li anode [2].

Most current battery designs suffer from either a low capacity or a reduction of capacity as the battery

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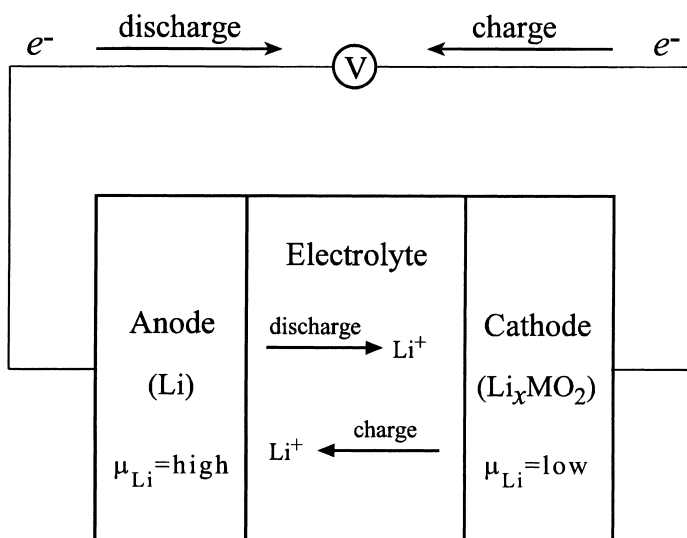


Fig. 1. Schematics of a rechargeable lithium battery.

is repeatedly charged and discharged. A complete picture of all the mechanisms that contribute to battery degradation for secondary lithium batteries does not yet exist, but obvious problems such as electrolyte breakdown have been clearly identified [3]. Battery degradation may also be associated with the metal oxide on the cathode side. The stability of the lithium-metal oxides in the demanding battery environment is highly questionable, and much of the technology may rely on the kinetic limitations for converting metastable phases into stable compounds. For example, many Li_xMO_2 compounds (where M is a 3d-transition metal) become highly oxidizing as Li is removed, and it is likely that under ideal equilibrium conditions these materials would lose oxygen [4]. In addition, in some lithium-metal oxides, phase transitions occur when Li ions are removed or inserted [5–10]. The accompanying volume changes can lead to mechanical failure of the cathode particles [11].

In this paper we investigate one particular instability, namely, the possible reduction of the metal ion instead of the lithium ion upon charging of the battery. In the charging cycle of the battery, the cathode is at positive potential with respect to the anode. In principle, a high enough potential will ultimately reduce all cations by driving them to the anode. Our objective is to investigate whether the equilibrium potential at which the transition metal is

reduced from Li_xMO_2 is below the reduction potential for lithium (which is the potential at or above which the battery has to be charged).

Using first-principles computations, to determine the relevant reaction energies, we find that in many cases it is thermodynamically favorable to extract the metal from the Li_xMO_2 compounds and deposit it on the anode, rather than the Li ions. Although kinetic limitations may prevent this in many battery designs, these results point at a clear inherent thermodynamic instability of current lithium-metal oxide electrode materials.

2. Methodology

First-principles methods are finding considerable applications in the battery materials field [12–18]. Recently, we developed a method to predict the average potential at which Li intercalates into a given metal oxide, and used it to systematically study the factors that influence the intercalation voltage [12–14]. As our method is based on first-principles quantum mechanical techniques, it does not require any experimentally measured input data. It can therefore be used to study novel or hypothetical materials, or difficult to investigate reactions.

The open-cell voltage (OCV) of a Li battery is directly proportional to the chemical potential differ-

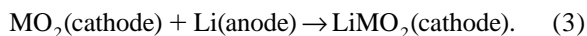
ence for Li in the anode and in the cathode (with composition Li_xMO_2),

$$V(x) = -\frac{\mu_{\text{Li}}^{\text{Cathode}}(x) - \mu_{\text{Li}}^{\text{Anode}}}{zF} \quad (1)$$

where F is the Faraday constant and z is the charge associated with Li displacement from the electrode (for Li, $z=1$). The open cell voltage is often erroneously related to the difference in work functions between the anode and cathode [19,20]. This is incorrect as it neglects the contribution of the Li^+ ion in the electrochemical reaction [21]. Since the chemical potential in the lithium-metal oxide on the cathode depends on the amount of Li already present, the open-cell voltage varies as a function of the depth of the charge or discharge. Although the methodology for computing $\mu_{\text{Li}}^{\text{Cathode}}(x)$ exists [16,22–24], its calculation is time consuming; so rather than calculate the OCV as a function of x we determine the *average* OCV over a full charge/discharge cycle. By simply integrating Eq. (1) between compositions MO_2 and LiMO_2 one obtains the standard Nernst equation for the average OCV [12]:

$$\bar{V} = \frac{-\Delta G_r}{F} \quad (2)$$

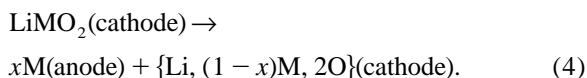
where ΔG_r is the Gibbs free energy for the reaction:



Although full deintercalation to composition MO_2 is not realistic for all choices of the metal M, the *average* OCV determined this way is still a good indication for the Li-intercalation potential. As Eq. (3) indicates, we chose the anode chemical potential as that of Li metal in the BCC structure. This choice is not important since another anode (e.g. lithium dissolved in graphite) would only shift the average voltages by a constant amount. Volume effects and entropic effects are minimal in the intercalation reaction, Eq. (3), so that the change in Gibbs free energy can be approximated by the change in internal energy (ΔE_r) at 0 K. The term $P\Delta V_r$ is of the order 10^{-5} eV whereas ΔE_r is of the order of 3 to 4 eV per molecule. The term $T\Delta S_r$ is of the order of the thermal energy, $k_B T$, which is about 0.025 eV at room temperature and much smaller than ΔE_r . Eq.

(2) shows how by computing the energy of two compounds and metallic Li, we can obtain the *average* Li-intercalation potential for a system. To compute the energy of the compounds in Eq. (3) we use the first-principles pseudopotential method [25–27] which has been found to be highly reliable for oxides [28–32]. From the reaction energy the average OCV is obtained. The advantage of this procedure is that no experimental input is required. It is thus possible to determine quickly the *average* OCV for new compounds, or existing compounds in other structures. Recently we used this approach to investigate how structure and composition independently affect the potential at which Li intercalates [12].

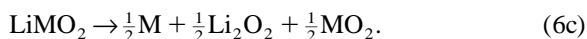
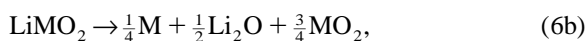
The same approach can be used to estimate the voltage at which the M ions would be extracted from the cathode. Metal extraction and reduction may be given by the general reaction:



$\{\text{Li}, (1-x)\text{M}, 2\text{O}\}$ could be any product (single or multiphase) with the correct composition. It is difficult to estimate the products of such reactions, but any reasonable product can serve to provide an *upper bound* for the reduction potential of the M ions. The average reduction potential for the metal M can again be obtained by applying the Nernst equation to reaction (4):

$$V_M^{\text{reduction}} = \frac{G_{\{\text{Li}, (1-x)\text{M}, 2\text{O}\}} + xG_M - G_{\text{LiMO}_2}}{xzF}. \quad (5)$$

The most stable $\{\text{Li}, (1-x)\text{M}, 2\text{O}\}$ product will result in the lowest reaction free energy and therefore give the lowest reduction potential. Any other product (real or hypothetical) will give an upper bound for the thermodynamic equilibrium potential. In this paper we will calculate the reaction energy for three hypothetical solid state reactions which include metal reduction.



Whereas reactions (6b) and (6c) contain known

lithium oxides, reaction (6a) contains the hypothetical LiO_2 compound which is derived by removing the M ions topotactically from LiMO_2 in the α - NaFeO_2 structure. Because the charge transfer associated with the metal reduction is unknown, we will present the results for different values of z ($z=1, 2$ and 3) in Eq. (5).

The total energy of all compounds in this study was calculated with the pseudopotential method as implemented in the VASP program [26,27,33] with exchange and correlation in the Local Density Approximation. In this method only the valence electrons are taken into consideration and the effect of nucleus and core electrons are represented by the pseudopotential. The wave functions of the valence electrons are expanded in plane waves. VASP uses ultrasoft pseudopotentials which allow the use of moderately low energy cutoffs for the expansion of the plane waves. In this study, the energy cutoff for plane waves was set to 600 eV. The reciprocal space sampling was done with 116 k -points for the oxides and 256 k -points for the metals in the irreducible Brillouin zone.

We used the α - NaFeO_2 structure (space group $R\bar{3}m$) for all LiMO_2 and MO_2 compounds, the FCC structure for the reduced metals Ti, Co and Ni, and the BCC structure for V, Mn and Fe. Li_2O adapts an antiperovskite cubic structure (space group $Fm\bar{3}m$) and Li_2O_2 has a hexagonal structure (space group $P\bar{6}$). For the hypothetical LiO_2 compound we topotactically removed the M ion from the LiMO_2 compound in the α - NaFeO_2 structure. All the degrees of freedom in the structures were relaxed to find the minimal energy. The calculated lattice parameters for the experimentally observed structures are 3–4% smaller than the experimental values as expected in LDA calculations. In some cases the structures we used are not the equilibrium phase of the material, but structural differences generally affect the voltages by less than half a volt [12,13,15]. For example, the voltage of LiCoO_2 in α - NaFeO_2 and γ - LiFeO_2 structures differ by 0.49 eV [12] and the voltage of LiMnO_2 in α - NaFeO_2 and spinel structures differ only by 0.09 eV [13]. The change in total energy for the metallic elements is even less than the values given above [34,35]. Given that we only want to obtain qualitative information these assumptions seem therefore justified.

3. Results and discussion

Fig. 2 shows the calculated reduction potential for the metal and lithium ion in various LiMO_2 compounds for $z=1, 2$ and 3 . Note that for almost all metals, Eq. (6c) is favored thermodynamically, except for Ti, where the formation of Li_2O is more likely as a reduction product. For $z=1$, Fig. 2(a), the average reduction potential for all metals (except Ni) and all possible reaction products considered, are above the average lithium reduction potential, indicating that the metals may be stable against reduction. For $z=2$, Fig. 2(b), the reduction potentials of the late transition metals fall below that of the lithium reduction curve. The lithium oxides of Mn, Fe, Co and Ni are thermodynamically less stable to metal reduction than Ti and V. This effect is more pronounced for the more stable reaction products, Eq. (6b) and Eq. (6c). In Fig. 2(c) ($z=3$) it can be seen that, for the most stable reaction products, the metal reduction potentials are always below the lithium reduction potentials. However, such a high valence state of the metal ions in organic electrolytes may be unlikely. Although reaction (6a) gives the least stable products on the cathode and therefore the highest reduction potential, it may be the easiest reaction to achieve. Both reactions (6b) and (6c) require major rearrangement of Li and O ions. Reaction (6a), however, only requires the topotactic removal of the M-ions from the α - NaFeO_2 structure. Although this is unlikely to happen throughout the bulk of the material, due to the very low diffusivity of the M cations, it may occur rapidly near the surface of the particles, once the critical charging potential is reached.

While the results indicate that M reduction upon charging is possible, other potential degradation mechanism can be identified by combining Eqs. (3) and (6). Of particular interest are corrosion reactions which require no external current flow. The above results show that, for some choices of metal M, that the metal reduction potential is lower than the lithium potential. One can, then, envisage a reaction in a charged battery in which lithium ions spontaneously move from the anode into the cathode (lithium oxidation), meanwhile compensated by an opposite flow of metal ions (metal reduction). Clearly, Fig. 2 indicates that there is a net driving force

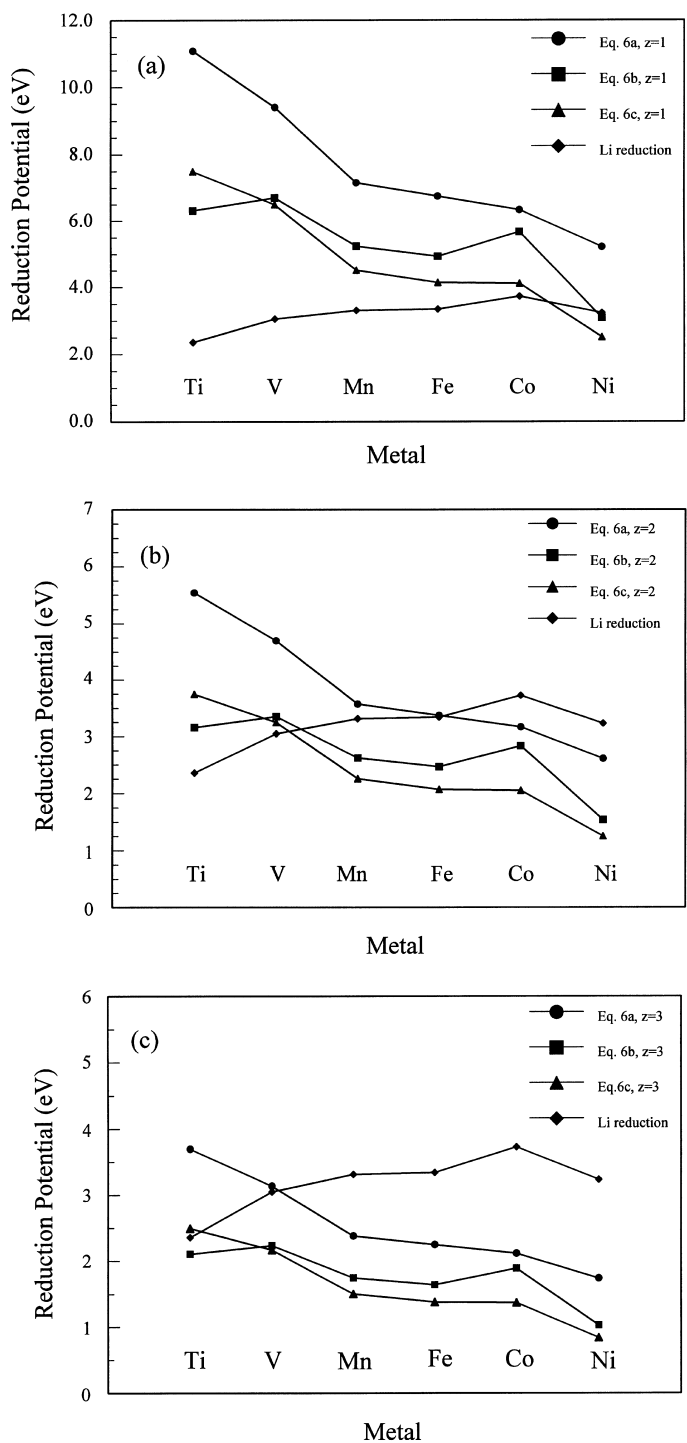


Fig. 2. Lithium and metal reduction potentials in LiMO_2 compounds using the reduction reactions in Eqs. (6a)–(6c). Metal reduction potentials are given for (a) 1+, (b) 2+ and (c) 3+ valence state of the metal.

for this reaction to take place. This would lead to a spontaneous self-discharge of the battery accompanied by loss of capacity.

The approximations we made in the above calculations are in most aspects conservative towards metal reduction. The somewhat arbitrary choice of reaction products in Eq. (6) leads to an overestimate of the reduction potential. In reality, reduction may therefore occur at an even lower potential. In particular, if the formation of O_2 gas is allowed, it is likely that lower energy reaction products can be obtained.

Another approximation comes from the fact that we computed the *average* potential over the full reduction cycle, i.e. the average potential in going from $LiMO_2$ to MO_2 (for lithium reduction) or to $\{Li, (1-x)M, 2O\}$ (for M reduction). When starting from the $LiMO_2$ stoichiometry both the lithium and metal reduction potential will be below the average value for the full displacement cycle. As charging occurs, Li is removed and its reduction potential increases. As long as no metal ions are removed the metal reduction potential will stay below its average value. The strongest driving force for metal reduction will therefore occur at the end of charge when the voltage required for lithium reduction potential is highest. Even when the *average* metal reduction potential is higher than the *average* lithium reduction potential, it is, therefore, still possible to have metal reduction at the end of the charging cycle.

Recently Amutucci et al. [36] presented evidence for metal reduction in $LiCoO_2$ cells. After charging a cell up to 4.5 volts they found significant amounts of Co deposited on the anode. In addition, the amount of Co at the anode was found to be directly proportional to the capacity loss in the cell indicating that metal reduction is an important failure mechanism in $LiCoO_2$ cells. The results of our calculations corroborate this failure mode of $LiCoO_2$ cathodes. Similar evidence for Mn deposits at the anode of cells with $LiMn_2O_4$ cathodes has also been found [37,38] and related to the capacity loss observed in this system [38].

Our calculations indicate which ion is thermodynamically favored to be reduced first upon charging. The rate at which this reduction occurs will depend strongly on the kinetic factors that control it. The diffusivity of the metal ions in the intercalation oxides is likely to be several orders of magnitude

below that for Li^+ ions. However, the biggest barrier to metal reduction is more likely the limited solubility of the higher valent metals in the electrolyte. If the ions can not dissolve in the electrolyte they cannot reach the anode, effectively blocking the reduction reaction of Eq. (4). As the reactions of Eq. (6) only involve products on the anode and cathode, our results are independent of the electrolyte. The rate at which they occur will, however, definitely depend on the choice of electrolyte. The possibility of a redox reaction between the cathode and electrolyte should also not be excluded as a source of battery degradation. Our results only point at one possible degradation mechanism.

4. Conclusion

First-principles comparisons of the metal reduction and lithium reduction voltages in layered $LiMO_2$ compounds point at an intrinsic instability of these materials towards reduction of the metal ion. We find that for $M=Mn, Fe, Co$ and Ni the metal ion is thermodynamically unstable against reduction during all or part of the charge cycle. This may be a significant contribution to the observed capacity loss of cells constructed with these high energy-density electrodes. Moreover, we predict that a charged battery can self-discharge by an ion exchange mechanism. The results also point at an important secondary role for the electrolyte. An electrolyte should have very low solubility for these metal ions, as blocking metal diffusion in the electrolyte may be the only way of effectively preventing the capacity loss due to metal reduction. Solid polymer electrolytes may in this respect have an advantage over liquid electrolytes.

Early transition metal oxides Ti and V are less prone to metal reduction during charging, at least for the reduction products we have investigated. Ti containing cathode materials, in this respect, can be good candidates for secondary lithium batteries.

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