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To cite this article: Hong Li et al 2004 J. Electrochem. Soc. 151 A1878

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Journal of The Electrochemical Society, **151** (11) A1878-A1885 (2004) 0013-4651/2004/151(11)/A1878/8/\$7.00 © The Electrochemical Society, Inc.



Li-Storage via Heterogeneous Reaction in Selected Binary Metal Fluorides and Oxides

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We report on electrochemical reactions of a variety of metal fluorides (TiF₃, VF₃, MnF₂, FeF₂, CoF₂, NiF₂, CuF₂, CaF₂, BaF₂), metal oxides (TiO, TiO₂, VO₂, V₂O₃, V₂O₅, NbO, NbO₂, Cr₂O₃, RuO₂, MoO₃), TiS₂, and TiN with lithium in nonaqueous lithium cells over a wide voltage range (0.02-4.3 V) at room temperature. In most cases, deep Li uptake occurs via heterogeneous reaction resulting in transformation of MX_m (M = transition metal; X = F or O or S or N) into a nanocrystalline or amorphous LiX_{m/n}/M composite from which Li can be extracted under restoration of the MX_m phase. Thermodynamic and kinetic aspects, especially overpotential and its possible origins for both Li uptake and Li extraction processes, are discussed. © 2004 The Electrochemical Society. [DOI: 10.1149/1.1801451] All rights reserved.

Manuscript submitted December 29, 2003; revised manuscript received March 24, 2004. Available electronically October 21, 2004.

Chemical energy can be reversibly stored in lithium rechargeable batteries through homogeneous intercalation and deintercalation reactions without significant structural changes.¹⁻³ Such "Li-ion batteries" show excellent cyclic performance. However, the number of available sites in the host lattice and the redox competition with other phases limit the Li storage capacity. For example, not more than 0.5 Li can be extracted from LiCoO₂ (cathode), and the Li content in graphite (anode) is limited by the composition LiC₆, corresponding to storage capacities of 145 and 372 mAh/g, respectively.^{2,3}

Heterogeneous Li uptake reactions have also been applied for energy storage, but mainly in primary batteries, of Li/MnO₂ and Li/(CF_x)_n batteries. The insertion of lithium into MnO₂ and (CF_x)_n (x = 1) leads to the formation of Mn/Li₂O and C/LiF composites. Li-storage capacities are as high as 1230 mAh/g for MnO₂ and 890 mAh/g for (CF_x)_n. The open-circuit voltages of the batteries are around 3 V. Consequently, these batteries possess high energy densities of 250-320 Wh/kg.^{2,3} (Besides these two materials, many other compounds were investigated with respect to their use in primary lithium batteries.) Li storage in these systems is not reversible, mainly due to the inactivity of Li₂O and LiF. Therefore, heterogeneous Li uptake reactions have not attracted much attention in earlier times with regard to rechargeable lithium batteries.

Recently, Poizot *et al.*⁴ found that a far-reaching reversible Li storage can be achieved in several transition metal oxides (M = Fe, Ni, Co, Cu) by a reduction to the metal. The detailed studies show that a corresponding uptake of Li transforms the transition metal oxide into a M/Li₂O nanocomposite in which 2-5 nm metal grains are embedded in an amorphous Li₂O matrix.^{4,5} The process of Li uptake/extraction is reversible in a voltage range of 0-3 V with about 75% coulombic efficiency at the first cycle and nearly 100% coulombic efficiency in the following cycles. These transition metal oxides show high reversible Li storage capacities of 400-1000 mAh/g and good cyclic performance with an average Li uptake voltage of 1.8-2.0 V. The reason Li₂O shows such an unusual reactivity at room temperature in these cases is believed to be related to the formation of extremely small separation distances between Li₂O and metal nanograins.⁴

This finding is of high technological relevance. It points out that a reversible Li storage can be also achieved by heterogeneous uptake. Similar to transition metal oxides, we have also found that transition metal fluorides (TiF₃ and VF₃) show such an electrochemical reaction mechanism with Li (500-600 mAh/g reversible capacity) at room temperature.⁶ Independently, Badway *et al.* dem-

onstrated that also FeF₃ mixed uniformly with carbon black exhibits a reversible capacity of 600 mAh/g at 70°C.^{7,8} These results imply that the nanocrystalline or amorphous mixture of LiF/M exhibits electrochemical activity even at room temperature.

In view of practical applications, however, the performance of the reported materials is not very satisfactory. Coulombic efficiency at the first cycle is less than 75% for most other materials.⁴⁻⁶ Fortunately, this heterogeneous storage mechanism is not necessarily connected with low coulombic efficiency. Such an exception was found by Balaya *et al.*⁹ In the case of RuO₂, 98% coulombic efficiency was reported for the first cycles with a reversible capacity of 1110 mAh/g in the voltage range of 0.05-4.3 V and 99% coulombic efficiency with a capacity of 730 mAh/g at 0.8-4.3 V.⁹

An appropriate anode material should exhibit low voltage while a cathode material should exhibit a high voltage vs. Li⁺/Li. However, materials studied so far with respect to the heterogeneous mechanism show moderate average working voltage and a wide voltage range. This would be equivalent to a low energy density if used in batteries (*e.g.*, the energy density of the $Co_3O_4/LiCoO_2$ battery is 120 Wh/kg, less than 180-220 Wh/kg of graphite/LiCoO₂ type Li-ion battery¹⁰).

For a deeper understanding of the behavior of this unusual heterogeneous Li storage phenomenon, as well as for a better material selection, systematic work on thermodynamic and kinetic aspects of the heterogeneous solid-state uptake/extraction reaction is necessary. In this paper, we report part of our investigations on the electrochemical reactions of selected metal fluorides and oxides with lithium.

Thermodynamic Considerations

The overall Li uptake and Li extraction from a binary metal compound MX_n under investigation (X =F, O, S, N) can be written as

$$n\text{Li} + MX_m \rightleftharpoons M + n\text{Li}X_{m/n}$$

$$(m = n \text{ for } X = F, N; m = n/2 \text{ for } X = O, S)$$
[1]

For such a reaction, the values of the cell voltage [electromotive force (emf)] can be calculated using the Nernst equation

$$\Delta G = n \Delta G_{\rm f}^{\circ}({\rm LiX}_{\rm m/n}) - \Delta G_{\rm f}^{\circ}({\rm MX}_{\rm m}) = -nEF \qquad [2]$$

The theoretical emf values (*E*) and the theoretical Li storage capacities for Reaction 1 of a variety of MX_m (X = F, O, S, N) compounds are listed in Table I. Free energy data for these materials at 25°C are taken from the literature.¹¹ EMF values are calculated from Gibbs free energies of formation (ΔG_f) of LiX_{m/n} and the initial compounds MX_m . These emf values refer to a cell where Li activity is

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|---------------------|---------------------------|-------------|-----------------------------------|------------------|---------------------------|------------|-----------------------------------|--------------------------------|-------------------------|------------|-----------------------------------|
| MX | $\Delta_{ m f}G$ (kJ/mol) | EMF (V) | Li storage capacity (mAh/g) | MX | $\Delta_{ m f}G$ (kJ/mol) | EMF (V) | Li storage capacity (mAh/g) | MX | $\Delta_{ m f}G$ kJ/mol | EMF (V) | Li storage capacity (mAh/g) |
| LiF | -589 | | 0 | MnO ₂ | -465 | 1.708 | 1233 | Ga ₂ O ₃ | -998 | 1.188 | 858 |
| TiF ₃ | -1361 | 1.396 | 767 | Mn_2O_3 | -881 | 1.431 | 1018 | GeO ₂ | -521 | 1.562 | 1025 |
| VF ₃ | -1227 | 1.863 | 745 | MnO | -363 | 1.032 | 756 | Al_2O_3 | -1582 | 0.180 | 1577 |
| MnF_2 | -807 | 1.919 | 577 | FeO | -251 | 1.61 | 746 | MgO | -569 | -0.0354 | 1330 |
| MnF_3 | -1000 | 2.647 | 719 | Fe_2O_3 | -742 | 1.631 | 1007 | SiO_2 | -856 | 0.694 | 1784 |
| FeF ₂ | -663 | 2.664 | 571 | CoO | -214 | 1.802 | 715 | B_2O_3 | -1194 | 0.850 | 2300 |
| FeF ₃ | -972 | 2.742 | 712 | NiO | -212 | 1.954 | 718 | Ce_2O_3 | -1708 | -0.038 | 490 |
| CoF_2 | -627 | 2.854 | 553 | CuO | -128 | 2.248 | 674 | Li ₂ S | -439 | ••• | 0 |
| CoF ₃ | -719 | 3.617 | 694 | Cu_2O | -148 | 2.147 | 375 | TiS ₂ | -402 | 1.233 | 957 |
| NiF ₂ | -604 | 2.964 | 554 | ZnO | -320 | 1.252 | 659 | CoS_2 | -146 | 1.898 | 871 |
| CuF_2 | -492 | 3.553 | 528 | SnO | -257 | 1.566 | 398 | Co_3S_4 | -487 | 1.644 | 703 |
| ZnF_2 | -714 | 2.404 | 518 | SnO_2 | -520 | 1.582 | 711 | CuS | -53 | 1.998 | 561 |
| SnF_2 | -601 | 2.984 | 342 | Ag_2O | -11.2 | 2.855 | 231 | Cu ₂ S | -86 | 1.827 | 337 |
| AgF | -187 | 4.156 | 211 | RuO ₂ | -280 | 2.12 | 805.6 | FeS | -102 | 1.747 | 610 |
| PbF_2 | -617 | 2.903 | 218 | MoO_2 | -533 | 1.669 | 838.2 | FeS ₂ | -160 | 1.861 | 893 |
| CaF ₂ | -1173 | 0.0259 | 686 | MoO_3 | -668 | 1.75 | 1117 | MnS | -218 | 1.144 | 616 |
| BaF_2 | -1158 | 0.104 | 306 | SrO | -561 | 0.005 | 517 | MnS_2 | -225 | 1.692 | 900 |
| Li ₂ O | -562 | | 0 | SrO_2 | -573 | 1.428 | 896 | MoS_2 | -226 | 1.69 | 670 |
| TiO | -513 | 0.253 | 839 | Y_2O_3 | -1817 | -0.226 | 712 | Ag_2S | -40.7 | 2.06 | 216.3 |
| TiO ₂ -R | -890 | 0.608 | 1342 | ZrO_2 | -1040 | 0.217 | 870 | Li ₃ N | -129 | ••• | 0 |
| TiO ₂ -A | -883 | 0.625 | 1342 | NbO | -392 | 0.881 | 492 | TiN | -309 | -0.623 | 1301 |
| VO | -404 | 0.819 | 801 | NbO_2 | -795 | 0.852 | 858 | Co ₃ N | -34 | 0.326 | 421 |
| V_2O_3 | -1139 | 0.945 | 1073 | Nb_2O_5 | -1766 | 1.082 | 1008 | Fe ₄ N | -3.722 | 0.432 | 338.7 |
| VO_2 | -1318 | -0.502 | 1293 | In_2O_3 | -831 | 1.477 | 579 | Mn_4N | -105 | 0.083 | 459 |
| V_2O_5 | -1419 | 1.441 | 1474 | Sb_2O_3 | -634 | 1.817 | 552 | Mn_5N_2 | -155 | 0.176 | 531 |
| Cr_2O_3 | -1058 | 1.085 | 1058 | PbO | -189 | 1.933 | 721 | | | | |
| Cr_3O_4 | -1531 | ~ 0.93 | 975 | CeO ₂ | -1025 | 0.257 | 623 | | | | |

Table I. EMF values, Gibbs free energy of formation ($\Delta_{f}G$), and Li storage capacities for binary metal compounds.

given by Li metal on one side and by the three-phase contact of $\text{LiX}_{m/n}$, MX_m , and M on the other side. In doing so we obviously neglect the influence of Li solubility on the chemical potential of MX_m . This is justified if the solubility is small and is grossly incorrect if a compound formation occurs. According to Table I, except VO_2 , Y_2O_3 , MgO, and TiN, the emf values are in the range of 4.2-0 V. It means that Reaction 2 is thermodynamically feasible for non-aqueous electrolyte systems. Table I also shows that some materials exhibit high theoretical Li-storage capacities above 600 mAh/g.

Figure 1 displays, for different transition metal oxides and fluo-



Figure 1. Calculated emf values for a deep Li uptake into MX_m (X = F, O). Also compared with the working voltage of some Li-intercalation compounds as cathode in Li ion batteries.

rides, the trend of the emf values with increase in the atomic number of the transition metals. As expected, the emf values increase from Ti to Cu for the compounds with the same stoichiometry and also increase with the oxidation state for the same metal. The working voltages of some well-known Li-intercalation compounds are listed for comparison. According to this figure, CuF_2 , CuF, CoF_3 , CoF_2 , NiF_2 , FeF_3 , FeF_2 , and MnF_3 are suitable as cathode materials, while VO and TiO are suitable as anode materials.

The uptake of Li by MX_m may process through multiple-step reactions. For example, the insertion of Li into TiF₃, VF₃, FeF₃, or RuO₂ leads to the intermediate formation of complex compounds such as $\text{Li}_x MX_m$.⁶⁻⁹ In highly oxidized materials, the formation of $M/\text{Li}X_{m/n}$ could occur through several steps, *e.g.*, CuO is converted to Cu/Li₂O upon uptake of Li through the formation of Li_xCuO and subsequently, of Cu₂O.^{5,12} In such cases, multiple plateaus are expected in the U(x) profiles (U is the cell voltage and x is the amount of Li uptake).

Strictly speaking, Eq. 2 is only effective for bulk material. For material at nanoscale, an extra surface/interface energy contribution should be taken into consideration that may be approximately written as^{13}

$$\Delta_{\rm r}G = -nEF = \Sigma_{\rm i}\Delta_{\rm f}G_{\rm i}(r=\infty) + 2\Sigma_{\rm i}\bar{\gamma}_{\rm i}V_{\rm i}/\bar{r}_{\rm i} \qquad [3]$$

where $\bar{\gamma}$ is the effective surface tension, V is the partial molar volume, and \bar{r} is the effective grain radius. In a case that grain size of the material is 1 nm, emf value may be modified about 100 mV or less.¹³ Because most materials listed in Table I show high emf values above 1 V, such an influence is not important.

Experimental

The materials studied here are TiF_3 , VF_3 , FeF_2 , FeF_3 , MnF_2 , MnF_3 , CoF_2 , NiF_2 , CuF_2 , BaF_2 , CaF_2 , TiO, TiO_2 (anatase), TiS_2 , TiN, NbO, Nb_2O_5 , V_2O_3 , VO_2 , Fe_2O_3 , RuO_2 , and MoO_3 , all of



Figure 2. Voltage profiles of current collector Ti foil (A) and conductive additive carbon black (CB) and graphite (1:1 in weight ratio) in a lithium cell. Io = $25 \ \mu$ A/cm² for (a) and Io = $0.15 \ m$ A/cm² for (b).

them being used as purchased (Alfa-Aesar, 98-99%). Electrochemical experiments were performed using Swagelock-type twoelectrode cells. The working electrodes were composed of metal fluorides/oxides, carbon black, graphite, and poly(vinylidene difluoride) (PVDF) at a weight ratio of 10:1:1:1 unless mentioned specifically. The mixture was pasted on pure Ti foil (99.6%, 30 μ m thickness, Goodfellow) and Celgard 2300 used as separator. The electrolyte consisted of 1 M LiPF₆ dissolved in ethylene carbonate (EC) and dimethyl carbonate DMC (1:1 in volume, Merck). Pure lithium foil (Aldrich) was used as counter electrode. The batteries were assembled in a MBraun glove box (H₂O < 2 ppm).

The discharge and charge cycling was performed under a constant current density of 0.15 mA/cm² at a voltage range of 0.02-4.3 V using an Arbin MSTAT system at room temperature. Powder X-ray diffraction (XRD) patterns were recorded in a Philips machine (PW 3020, Cu K α radiation).

Results and Discussion

Discharge and charge behavior.—In order to study the electrochemical behavior of the materials in a wide electrochemical window (0.02-4.3 V), Ti foil is used as current collector (upper limit of 4.3 V is to avoid decomposition of the electrolyte). Discharging and charging curves of pure Ti foil given in Fig. 2a show that the Listorage capacity of the Ti foil is small, in the range 0-4.3 V. It is known that Li cannot alloy with Ti. The observed residual capacity may be caused by the decomposition reaction of the electrolyte or by electrochemical reactions of trace amount of surface oxide on Ti foil. Compared to the capacity of active electrode materials, which is in the range of 500-1000 mAh/g as discussed later, the contribution of the Ti foil to the voltage profiles can be ignored. A mixture of carbon black and graphite at a weight ratio of 1:1 is used in some of the cases as conductive additive. The electrochemical performance of the conductive additive is displayed in Fig. 2b.

Typical discharge and charge curves of transition metal fluorides (M = Ti, Ni, Cu) are shown in Fig. 3a-c. During first discharge, while TiF₃ and NiF₂ exhibit at least one plateau at rather high potential, CuF2 exhibits two plateau regions similar to CuO.^{5,12} Following these plateau regions, one sloping behavior is distinctly observed in their voltage profiles at the low potential of first discharge. A plateau in the voltage profile is generally an indication of a phase transformation reaction. For most of the materials, the capacities corresponding to the plateau at the first discharge are close to the values calculated from Reaction 1. Therefore, the plateau at the first cycle in Fig. 3 is attributed to Reaction 1. The sloped region at low voltage denotes an extra Li storage capacity of 200-300 mAh/g during discharging and 100-200 mAh/g during charging. During the charging process, besides a sloped region at low voltage, at least one voltage plateau can be clearly observed in several materials investigated here and attributed to Reaction 1. In this paper, we focus our discussion on the capacity due to decomposition reaction in the voltage range 4.3-0.5 V. Hence, we ignore the additional contributions due to the conductive additive. In addition, the extra reversible capacities due to Li storage in the newly formed LiX/M boundaries at sloped regions will be considered in more detail in a forthcoming publication.14

Comparing the voltage profiles in Fig. 3a-c for discharging, a large capacity loss is observable in the plateau region for most of the fluorides during the first cycle due to nonreacted LiF. After the first cycle, the depth of Li during discharge and charge fades slowly in the cases of TiF_3 and VF_3 (see Ref. 6) and more quickly in the other fluorides.

The Li-uptake/extraction described by Eq. 1 has been confirmed directly by XRD, high-resolution transmission electron microscopy (HRTEM), and Raman spectroscopy in the cases of CuO, Cu₂O, CoO, Co₃O₄, Fe₂O₃, RuO₂, TiF₃, VF₃, and FeF₃.^{4-10,15-18} The voltage profiles for most of the other materials which we investigated are similar to those shown in Fig. 3; therefore, we assume the same mechanism to be operative in all these cases.

The Li uptake/extraction capacities at the plateau regions during discharging and charging for some transition metal compounds are listed in Table II. For fluorides, full Li uptake (according to Eq. 1) can be completed for all compounds and the Li extraction capacity is relatively large for TiF₃ and VF₃ but less for all the other fluorides investigated. In the case of the oxides, full Li uptake seems to be difficult for TiO₂ and V₂O₃, and the Li-extraction capacity decreases also from Cr to Cu.

In order to evaluate the reactivity of Li uptake and extraction reactions for different materials, two ratios are defined. R_A is a ratio of real Li uptake capacity during first discharge (excluding the capacity at the sloped region at low voltage) to the calculated capacity according to Reaction 1. If the ratio equals 1, it means that Li is consumed stoichiometrically according to Reaction 1. R_B is the ratio of real Li extraction capacity during first charge (excluding the capacity at the sloped region at low voltage) to calculated Li extraction capacity (equal to calculated Li insertion capacity). The subtraction of the capacity of the sloped region at low voltage is to highlight that the Li uptake/extraction capacity is due to the solid-state reaction as described in Eq. 1, as we do not consider the interfacial storage in this paper.

Figure 4a shows a summary of the relationship between theoretical emf values and the ratio R_A of binary metal compounds for Li uptake reaction, including some data calculated from the



Figure 3. Voltage profiles of MF_m in lithium cells at a range of 0-4.3 V: (a) TiF₃, (b) NiF₂, and (c) CuF₂. Electrode composition: active material CB; graphite PVDF (10:1:1:1). Io = 0.15 mA/cm².

references.^{4,12,16-18} The results in Fig. 4a indicate that if the emf value is above 1 V vs. Li⁺/Li, the ratio is close to or larger than 1 (*i.e.*, almost complete uptake). Only V₂O₅ and TiS₂ somehow drop out of this systematic behavior. On the contrary, materials with low emf values show a poor degree of Li uptake. The reader should note that the reasons for the R_A values exceeding unity is because the subtraction of interfacial contribution is imprecise in all cases and in few materials the SEI formation starts above 0.8 V.

Similarly, Fig. 4b indicates the relationship between emf values and the extractability of Li. Because complete Li uptake according to Reaction 1 is obviously not possible for the materials with emf value less than 1 V, Li extraction (ratio $R_{\rm B}$) cannot be significant. With regard to extraction (see Fig. 4b), the following tendency can be noticed: materials with high emf values obviously show poor Li extraction capacity. $R_{\rm B}$ for RuO₂ exceeds unity as we have not considered the contribution due to SEI decomposition. A preliminary impression based on Fig. 4a and b is that a moderate emf value is a good prerequisite for achieving reasonable Li insertion and extraction capacities. Data cited from references were obtained under different discharging/charging modes; hence, the comparison in Fig. 4 is only semiquantitative.

Influence of overpotential.—Due to kinetic barriers, the cell voltage (U) is not only determined by emf (E) values but also influenced by overpotential (η)

$$U(x) = E(x) \pm |\eta(x)|$$
[4]

Note that $|\eta(x)|$ is due to the internal polarization processes. The correction changes sign and possibly also magnitude if we change over from a charge to discharge profiles and vice versa. Thus, if $|\eta_1|$ refers to overpotential during discharging and $|\eta_2|$ during charging, they may not be equal due to different kinetic processes. The voltage hysteresis of discharging and charging profile is equal to $(|\eta_1| + |\eta_2|)$. Note that the experiments described here are performed galvanostatically and that in order to avoid the oxidation of the electrolyte, or Li deposition, the voltage is limited to the window 0.02-4.3 V.

For heterogeneous Li uptake/extraction reaction, the microstructure and components vary significantly during charging and discharging. The polarization $|\eta(x)|$ varies correspondingly with the depth (x) of the Li consumption/extraction. In the coexistence regime, E(x) is almost constant (slight variation being argued by the surface tension term in Eq. 3). Obviously, if the overpotential is large, the voltage variation is significantly influenced by the kinetic terms and even prevent x from reaching the theoretical value (i.e., for $|\eta(x)| \approx |E(x)|$ the voltage of our galvanostatic experiment reaches the operating limit 0.02 or 4.3 V). Table III lists the overpotential values for the Li uptake reaction at the plateau region. Most of the materials show values around 1 V. Referring to Fig. 4a, materials with emf values less than 1 V, showing poor Li uptake capacity, can be simply explained by this experimental restriction, that may be overcome by either lowering the current density or by performing potentiodynamic intermittent titration technique measurements.1

Conversely, during extraction, the voltage now exceeds *E* by the magnitude of the overpotential, and Li cannot be fully extracted in the cases of CuF_2 or CoF_3 if the same overpotential of 1 V is assumed (U > 4.3 V; see Fig. 4b). As already mentioned, the low *E* compounds in Fig. 4a cannot be substantially delithiated because the Li uptake was insignificant. Evidently, a moderate emf is favorable for complete Li extraction reaction. Note that in Fig. 4b, with increasing E values the free energy needed to remove the lithium according to the back reaction of Eq. 1 also increases. How far this explains the trend observed (indicated by dashed line in Fig. 4b), or how far this is due to the transport properties of the oxides/fluorides or of the additives, is beyond the scope of this work and cannot be decided at the moment.

Table II. Calculated Li-storage capacity and real Li uptake and extraction capacities of transition metal fluorides and oxides for phase transformation reactions.

| MF_m | TiF ₃ | VF ₃ | CrF ₃ | MnF_2 | MnF ₃ | FeF ₂ | FeF ₃ | CoF_2 | NiF ₂ | CuF_2 |
|--------------------------|------------------|-----------------|------------------|---------|------------------|------------------|------------------|---------|------------------|---------|
| Calculated | 767 | 745 | | 577 | 719 | 571 | 712 | 553 | 554 | 528 |
| 1st D _{plateau} | 640 | 600 | | 700 | 800 | 750 | 800 | 580 | 650 | 640 |
| 1st D _{slone} | 300 | 330 | | 61 | 320 | 300 | 320 | 270 | 350 | 220 |
| 1st D _{total} | 940 | 930 | | 761 | 1120 | 1050 | 1120 | 850 | 1000 | 860 |
| Slope | 0.7- | 0.15- | | 0.43- | 0.47- | | 0.76- | 1.12- | 1.38- | 1.01- |
| voltage | 0.02 | 0.02 | | 0.2 | 0.02 | | 0.02 | 0.02 | 0.02 | 0.02 |
| range (V) | | | | | | | | | | |
| for | | | | | | | | | | |
| discharge | | | | | | | | | | |
| 1st C_{slope} | 200 | 280 | | 180 | 250 | 140 | 140 | 250 | 280 | 250 |
| 1st C_{plateau} | 550 | 400 | | 120 | 250 | 210 | 220 | 50 | 320 | 50 |
| 1st C_{total} | 750 | 680 | | 300 | 500 | 350 | 360 | 300 | 600 | 300 |
| Slope | 0-1.8 | 0-2.2 | | 0-4.0 | 0-4.0 | 0-4.0 | 0-4.0 | 0-2.8 | 0-3.0 | 0-4.0 |
| voltage | | | | | | | | | | |
| range (V) | | | | | | | | | | |
| for charge | | | | | | | | ~ ~ * | | ~ ~ * |
| MO_m | TiO ₂ | V_2O_3 | Cr_2O_3 | MnO* | Mn_2O_3 | FeO* | Fe_2O_3 | CoO* | NiO* | CuO* |
| Calculated | 1342 | 1293 | 1058 | 756 | | 746 | | 715 | 718 | 674 |
| 1st D _{plateau} | 150 | 0 | 1160 | 980 | | 750 | | 720 | 790 | 760 |
| 1 st D_{slope} | 150 | 350 | 0 | 267 | | 406 | | 280 | 197 | |
| 1 st D_{total} | 300 | 350 | 1160 | 1247 | | 1156 | | 1000 | 987 | 761 |
| Slope | 1.7- | 3-0.0 | Not | 0.1-0 | | 0.5-0 | | 0.75- | 0.5-0 | 0.7-0 |
| voltage | 0.02 | | clear | | | | | 0 | | |
| range (V) | | | | | | | | | | |
| for | | | | | | | | | | |
| discharge | | | | | | | | | | |
| 1st C_{slope} | 35 | 150 | 100 | 227 | | 318 | | 420 | 359 | 172 |
| 1st C_{plateau} | 171 | 0 | 650 | 415 | | 390 | | 330 | 287 | 185 |
| 1st C_{total} | 206 | 150 | 750 | 642 | | 708 | | 750 | 746 | 357 |
| Slope | 0-2.0 | 0-4.0 | 0-1.0 | 0-1.0 | | 0-1.5 | | 0-2.0 | 0-2.0 | 0-2.5 |
| voltage | | | | | | | | | | |
| range (V) | | | | | | | | | | |

for charge

Li uptake: mechanistic details.-Now we refer to materials that allow for a full Li uptake, viz. TiF_3 , VF_3 , MnF_3 , FeF_3 , CoF_2 , NiF₂, CuF₂. Upon incorporation of Li⁺ and e⁻ into the electrode at the contact area between the particle and the current collector, intermediate phases such as $Li_x MF_m$ (m = 2 or 3) are formed in some cases prior to decomposition. Upon further uptake, the reaction eventually leads to the formation and nucleation of LiF/M phases. These can be amorphous or nanocrystalline, depending on the partial conductivities. Li⁺ may migrate through LiX_{m/n}, along grain boundaries, and/or via the electrolyte (it is not clear during the formation of nanocomposite whether the electrolytes could protrude into the composite). If Li⁺ alone is mobile without significant transport of M^{n+} or $X^-,\mbox{ most likely an "amorphous <math display="inline">\mbox{Li}X_{m/n}/M$ phase" is formed; if both Li⁺ as well as Mⁿ⁺ or X⁻ are mobile during reaction, the product can separate into crystalline phases ("nanocrystalline $\text{LiX}_{m/n}/M$ composite"). For further reaction to proceed, this newly formed composite must be well conducting for Li⁺ or e⁻. While in the amorphous phase both Li^+ and e^- have to be mobile; in the nanocomposite it is sufficient for Li^+ to move through $LiX_{m/n}$ and the electrons to move via the metal states. HRTEM studies on TiF₃ and RuO₂ electrodes provide clear evidence for these two situations, where LiF/Ti amorphous mixture⁶ and Li₂O/Ru nanocomposite9 have been observed, respectively. In addition to these limiting cases, also partially crystalline composites may be realized (e.g., metal nanograins embedded in amorphous $LiX_{m/n}$, or vice versa, viz. $\text{LiX}_{m/n}$ nanograins embedded in amorphous metal).

Now we consider the compounds in Fig. 4a, TiO, NbO, NbO₂, V_2O_3 , and VO_2 which do not take up a significant amount of Li (no plateau for Reaction 1 has been observed during discharging under current conditions), irrespective of the fact that they have high elec-

tronic conductivity at room temperature.¹⁹ These materials do not exhibit a great driving force for reacting with Li, and the overpotential is sufficient to bring the voltage down to zero. In order to check the influence of overpotential upon reduction of particle size on the battery performance of the conducting materials, we ballmilled NbO under argon atmosphere for 24 h. As a result of this treatment, the peaks in the XRD pattern become significantly broad as shown in Fig. 5a. Obviously the grain size is reduced to 5 nm as estimated by the Scherrer equation; hence, the transport length decreased and probably the number of surface defects also increased. These features are definitely beneficial for the Li insertion process. In fact, with a current density of 0.05 mA/cm², the Li uptake capacity has increased upon ballmilling from 4 to 300 mAh/g, as shown in Fig. 5b and c and the plateau region can be clearly observed. Lowering the current density to 0.025 mA/cm² in the case of microcrystalline NbO (figure not shown) did not improve the Li uptake. Although the Li uptake capacity of ballmilled NbO is still less than the theoretical value of 492 mAh/g, the experiment demonstrates the strong influence of grain size on the overpotential.

One further common phenomenon has been noticed. With regard to discharging at the second and all successive cycles, the voltage is higher for the first cycle as shown in Fig. 3. In addition the plateau is no longer well defined in the second and successive discharge curves. According to Eq. 3, variations of the $(\overline{\gamma}_i/\overline{r}_i)$ term leads to modifications of the cell voltage as well as the shape of the discharge curves. In addition, the overpotential decreases with the grain size because of kinetic reasons. This result is consistent with the NbO ballmilling experiment mentioned previously. The drop in $|\eta|$ also seems to be sensitive to the amount of Li charge. Obviously the process that controls $|\eta|$ seems to be sensitive to the amount of charge incorporated during discharge processes in the second and



Figure 4. (a, top) Relationship between Li uptake capacity and emf values. Ratio R_A equals to real Li uptake capacity (excluding the capacity at the sloped region at low voltage) to the calculated capacity according to a deep Li uptake reaction. (b, bottom) Relationship between Li extraction capacity and emf values. Ratio R_B equals real Li extraction capacity (excluding the capacity at the sloped region at low voltage) to the calculated capacity (excluding the capacity at the sloped region at low voltage) to the calculated capacity for a complete Li extraction from corresponding LiX_{m/n}/M. The ratio discussed is based on the galvanostatic charging/discharging experiment under a constant current density of 0.15 mA/cm², except data reported in the references (4,12,16,17) where 0.2 C was used. The fact that R_A exceeds unity in some cases in Fig. 4a is ascribed due to imprecise subtraction of the SEI and interfacial contributions. Data cited from references were obtained under different discharging/charging modes and hence the comparison here is only semiquantitative.

following cycles. These explanations need to be confirmed based on *in situ* conductivity measurements, which will be performed in the future.

Another point is that among fluoride compounds tested here, TiF₃, VF₃, and FeF₃ form Li_xMF₃ during Li insertion.²⁰ Other fluorides do not form such intercalation compounds. In the case of anatase TiO₂ (200 nm), only 0.5 Li can be incorporated, leading to the formation of Li_{0.5}TiO₂; further Li uptake (4Li corresponding to a capacity of 1340 mAh/g can be consumed as per the calculation) is not possible as shown in Fig. 6. These results indicate that the formation of Li intercalation compound is not a crucial condition for full Li uptake. Even in a well-crystallized Li_{0.5}TiO₂ an extra storage of 150 mAh/g occurs at the sloped region, unrelated to the decomposition of Li_{0.5}TiO₂ as in the cases of other oxides. The reason for this extra storage is unclear and needs further careful investigation.

Table III. Overpotential for Li uptake reaction of several materials; overpotential values for Li-insertion reaction into MX_m .

| MX_m | Overpotential | MX_m | Overpotential | MX_m | Overpotential |
|------------------|---------------|---|---------------|-------------------|---------------|
| TiF ₃ | 0.5 | CuF ₂ | 1.53 | CoO ^a | 1.0 |
| VF ₃ | 1.63 | SnF_2 | 1.71 | NiO ^a | 1.45 |
| MnF ₃ | 2.09 | Cr_2O_3 | 0.94 | CuO ^a | 1.0 |
| FeF ₃ | 1.72 | MnO | 0.48 | RuO2 ^b | <1.17 |
| CoF_2 | 1.58 | FeO ^a | 0.8 | SnO_2 | 0.64 |
| NiF ₂ | 1.45 | Fe ₂ O ₃ ^c | 0.7 | Ag_2O | 0.82 |

^a Calculated from Ref. 15.

^b Calculated from Ref. 9.

^c Calculated from Ref. 17.

Li-extraction: mechanistic details.—While during Li uptake by metal fluorides those particles being in contact with the current collector transform into an electronically (and ionically) conductive $\text{LiX}_{m/n}$ /M composite first, in the case of Li extraction we can assume due to the formation of insulating MX_m at the expense of the



Figure 5. (a) XRD of NbO powder after ballmilling in argon atmosphere for 24 h; (b) voltage profiles of a NbO/Li cell, NbO without ballmilling, Io = 0.05 mA/cm^2 ; (c) voltage profiles of a NbO/Li cell, NbO after ballmilling, Io = 0.05 mA/cm^2 .



Figure 6. Voltage profiles of anatase/Li cell. Io = 0.15 mA/cm^2 .

metal, the electronic conduction is expected to become increasingly problematic. Thus, it can be stated that the degree to which ion and/or electron conductivity is important depends very much on mechanism, materials, distribution topology, and the geometry. This point is also reflected by sensitivity of the overpotential on distribution of the conductive additive.

Normally a powder electrode with a typical thickness of 50-100 μ m is composed of many layers of active particles (100 nm-10 μ m particle size) stacking from the current collector (contact layer) to the outside surface. We first discuss a situation where the electrode is composed of pure active particle MX_m without conductive additive while MX_m is a poor electronic/ionic conductor.

Figure 7 shows a voltage profile of a TiF_3/Li cell in which the working electrode does not contain conductive additive. During the first discharge a plateau region is clearly observed. However, the plateau for Li extraction cannot be detected during the charging process. It indicates that the internal electrode resistance increases fast and only a small amount of lithium is extracted. However, if enough conductive additive is added, good electrical contact is established for each particle so that all particles take part in the Li



Figure 7. Voltage profiles of a TiF_3 /Li cell in which TiF_3 electrode is composed of TiF_3 and PVDF at a weight ratio of 10:1 without conductive additive.



Figure 8. Voltage profiles of a TiF_3/Li cell in which TiF_3 electrode is composed of TiF_3 , carbon black, and PVDF at a weight ratio of 10:2:1.

extraction process, and the Li extraction capacity is augmented. Figure 8 shows a voltage profile of a TiF₃/Li cell in which the working electrode is mixed with carbon black at a weight ratio of 5:1. Here the voltage plateau for the Li extraction reaction is clearly visible and a large Li extraction capacity is achieved. The plateau capacity for Li insertion during the second cycle decreases only by 20% compared to the first cycle. It is a significant improvement compared to the performance shown in Fig. 7 for TiF₃ without conductive additive. A similar observation has also been made in Badway's study on FeF₃/C cathode material.^{7,8} Recently, Kang et al.²¹ have improved the coulombic efficiency of Co₃O₄ from 69 to 79% by coating Co₃O₄ with Ni using ballmilling, resulting in an enhanced decomposition of Li₂O during charging. It is argued that this enhanced extraction of Li is caused by the catalytic effect as well as by the reduced impedance due to the addition of Ni. These results indicate that maintaining good electric contact for all particles is substantial in a poorly conductive MX_m.

When good electronic contact is established for each particle and the electrolyte wet all the electrode particles, the reaction depth is determined by the transport properties of each particle itself.

Extraction of lithium from $\text{LiX}_{m/n}/\text{M}$ nanocomposite results in the formation of nanocrystalline MX_m , as evidenced from HRTEM. To be specific, extraction of Li from the amorphous mixture of LiF/Ti in the case of TiF₃ electrode and that from the nanocrystalline composite Li₂O/Ru in RuO₂ electrode results in the formation of nanocrystalline TiF₃ and RuO₂, respectively. There is no evidence in any material studied so far, of the formation of amorphous MX_m, as a result of Li extraction. Among the transition metal oxides and fluorides studied here as well as those reported in literature, only RuO₂ allowed for a complete extraction of Li (nearly 100% coulombic efficiency) in the first cycle, while in other materials only about 75% or less Li ions are extracted and the remaining fraction (about 25%) of Li ions are trapped forever within the host materials.

However, the extracted active Li ions show nearly 100% coulombic efficiency with no further capacity loss during the second and following discharge and charge cycles.

As discussed earlier, as a consequence of heterogeneous Li uptake there should exist four basic types of microstructure of $\text{LiX}_{m/n}$ /M mixture^{4-6,8,9} as shown in Fig. 9: both $\text{LiX}_{m/n}$ and M are nanocrystalline (referred as Sa); $\text{LiX}_{m/n}$ and metal uniformly dispersed at atomic level forming an amorphous structure (Sb); metal nanograins embedded in amorphous $\text{LiX}_{m/n}$ matrix (Sc); $\text{LiX}_{m/n}$



Figure 9. Four possible microstructures of $\text{LiX}_{m/n}$ /M obtained by a full Li insertion into MX_m.

nanograins embedded in amorphous metal (Sd) (see Fig. 9). Each of these types of microstructure may lead to a different Li extraction process. It is until now impossible to predict which type of microstructure prevails for a given system. This point depends on the diffusivity of Li, X, and M atoms within the matrix and the rate of nucleation of LiX and M phases among other parameters.

Upon first charging, Li has to be extruded from the amorphous or nanocrystalline M/LiX $_{m\!/\!n}$ composite. This requires Li^+ and e^- to be conducting. It is plausible that with the gradual growth of the interphase of MX_m, the extraction of electrons or Li ions from the interior of the particle becomes more and more difficult due to the increased transport length. The Li extraction reaction then stops at a depth where the carriers cannot be sufficiently transported through MX_m phase in the time scale of the experiment. This terminates the Li extraction reaction and results in a capacity loss at the first cycle. In the following cycles in which the microstructure is assumed to be invariant, the reversible heterogeneous Li uptake/extraction reaction may occur within this depth (availability zone). This may explain the fact that nearly for all observed fluorides and most of the oxides, a large capacity loss appears at the plateau region in the first cycle and that Li uptake/extraction capacities at the successive cycles are relatively low but do not fade as fast as in the first cycle. Similar considerations have been discussed in Ref. 22 for the mechanism of Li extraction/insertion concerning LiFePO₄. Another important issue refers to the mobility of either X^- or M^+ ions, which is necessary for the transport across the MX_m interphase to enable further growth of MX_m grains. This could even be rate-determining at room temperature in the case that the grain size of $\text{Li}X_{\text{m/n}}$ and M are relatively large.

Thus, electronic and ionic conductivities of the nanocrystalline $MX_{m}\!,$ grain sizes of $LiX_{m\!/\!n}$ and M, in addition to electronic wiring achieved by the conductive additive, are important factors for a complete Li extraction process from $\text{Li}X_{\text{m/n}}/M$ composite. However, in addition to the loss of Li at the plateau region discussed previously, a fraction of Li may be also lost due to the formation of stable solid electrolyte interphase (SEI), which is not discussed here.

For most metal fluorides, electronic conductivity data at room temperature are still not available. Known data from few references indicate that conductivity of these fluorides are relatively poor (for FeF₃, $\sigma = 10^{-17}$ S cm⁻¹ at 250 K).²³ This may be one of the reasons fluorides show poor Li extraction capacity. Recent studies indicate that RuO₂ shows 98% coulombic efficiency at the first cycle even without conductive additive.⁹ It is known that RuO₂ is a metallic conductor at room temperature with the highest electronic conductivity among all compounds presented in Fig. 4¹⁹ and reasonably high Li⁺ diffusion coefficient.²⁴ These results confirm that the intrinsic conductivity of MX_m particles is also important for complete Li extraction.

Conclusions

The variety of materials studied here together with those reported in literature clearly show that the heterogeneous Li uptake/extraction reaction can be quite reversible and can lead to a very high Li storage capacity. Even compounds such as LiF and Li₂O exhibit electrochemical reactivity at room temperature. Our studies make the microstructural evolution understandable and also the different role of the transport properties for Li uptake and extraction. In some cases, high overpotentials for Li uptake as well as for extraction limit the choice of the materials for practical applications. Only those with emf values in the range of 1.0-3.0 V are expected to achieve reasonable Li uptake and extraction capacities under the experimental conditions used for the materials shown in Fig. 4a and b. Improving the transport properties by doping, decreasing the particle size, modifying surface, optimizing microstructure in particular with respect to the distribution of the conductive additive, as well as increasing reaction temperature^{7,8} could be possible solutions to design appropriate cathode or anode materials. The interfacial phenomenon which is favorable for Li storage at low potential will be discussed in a forthcoming publication.¹⁴

Acknowledgment

The authors acknowledge Dr. J. Jamnik and M. Dollé for their critical comments and suggestions. We also thank G. Götz for the technical support for XRD.

The Max Planck Institute for Solid State Research assisted in meeting the publication costs of this article.

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