

Coulometric Titration of Substituted $\text{Li}_x\text{La}_{(2-x)/3}\text{TiO}_3$

M. Klingler, W.F. Chu and W. Weppner

Chair for Sensors and Solid State Ionics, Christian-Albrechts University
Kaiserstr. 2, D 24143 Kiel, Germany

Abstract. Compounds of the series $\text{Li}_x\text{La}_{(2-x)/3}\text{TiO}_3$ ($x = 0.14, 0.23, 0.32, 0.35$) as well as materials which are substituted with Pr, Tb, Cr and Fe were investigated by the coulometric titration method. The equilibrium potential as a function of δ_{Li} as determined by the coulometric titration measurements was fitted using the random solution model which takes into account the ionic configurational entropy and the electronic contributions to the chemical potential of lithium.

1. Introduction

The compound $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ was first reported by Kochergina in 1984 [1]. More detailed investigations on the structure and the ionic conductivity of $\text{Li}_x\text{La}_{(2-x)/3}\text{TiO}_3$ for $0.12 \leq x \leq 0.45$ are described in [2-6]. The limited stability of this material against high lithium activities was reported by Inaguma [3].

In this work, we report measurements of the coulometric titration curve in order to study the insertion and extraction behavior of this material.

2. Experimental

2.1. Sample Preparation. Samples were prepared following the solid state reaction method described by A.R. West [6]. The starting materials, TiO_2 (99.8%), La_2O_3 (99.99%), Li_2CO_3 (> 99%), were dried and heated in order to decompose the initially formed $\text{La}_2(\text{CO}_3)_3$. The powder mixture was pressed isostatically into cylinders of 6 mm in diameter and about 15 mm in height at 205 MPa. The sample pellets embedded in the calcined powder were then sintered twice in a covered platinum crucible at 1100 and 1200 °C. The crystal structure was verified by X-ray diffraction.

2.2. Coulometric Titration Measurements. Coulometric titration measurements were performed in three electrode electrochemical cells consisting of a 1 molar solution of LiClO_4 in PC as electrolyte and lithium pellets as counter and reference electrodes. LiClO_4 was previously dried under vacuum for several days and PC (puriss./Fluka) was

dried over small pills of lithium. The electrolyte solution was stirred with a rate of 90 rpm.

The sintered cylinders were cut into thin pellets of 250-350 μm in thickness by a diamond wire saw, and both surfaces were ground down to 50 μm . One side of the thin pellet was sputtered with a molybdenum layer of about 150 nm in thickness.

3. Results and Discussion

3.1. Unsubstituted Materials. Coulometric titration measurements were conducted at room temperature on samples with $x = 0.14, 0.23, 0.32$ and 0.35 . The equilibrium potential (with reference to lithium) versus the intercalated amount of lithium, δ , is plotted in Fig. 1.

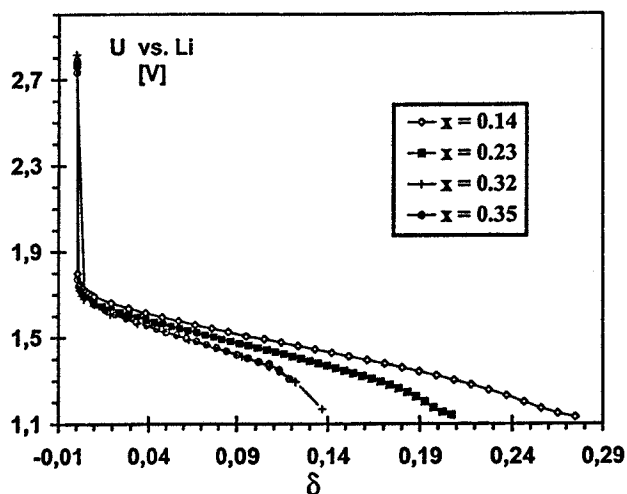


Fig. 1. Coulometric titration on $\text{Li}_{x+\delta}\text{La}_{(2-x)/3}\text{TiO}_3$.

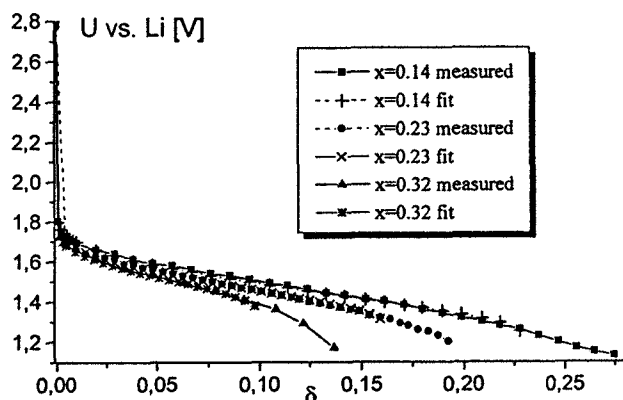


Fig. 2. Theoretically calculated and measured titration curves of $\text{Li}_{x+\delta}\text{La}_{(2-x)/3}\text{TiO}_3$.

The potential was taken under the condition that the decay of the potential was less than 2 mV/h for at least 1 h during the relaxation process.

In the case of insertion reaction electrodes, the electrode potential E as a function of δ can be written as

$$E = -\frac{\Delta H_{\text{ions}}}{n \cdot F} - \frac{R \cdot T}{n \cdot F} \ln\left(\frac{\delta}{\delta_x - \delta}\right) + A \frac{\delta^{2/3}}{m^*} \quad (1)$$

with the following notations:

- ΔH_{ion} : Enthalpy of the formation of $\text{Ti}^{3+}/\text{Ti}^{4+}$ ion pairs due to the Li^+ insertion/extraction,
 n : charge number of the ions,
 F : Faraday constant,
 R : gas constant,
 m^* : effective mass of electrons,
 δ_x : number of the effective available empty sites for Li^+ insertion,
 A : a materials constant,
as described by Raistrick et al. [7].

The second term at the right hand side of eq. (1) is due to the configurational entropy contribution of the ions and the last term is due to the electronic species.

Table 1. Parameters for the calculation of the cell voltage E .

x	$\frac{\Delta H_{\text{ions}}}{n \cdot F}$ [V]	maximal available vacancies	δ_x	A/m^* [V]
0.14	1.657	0.24	0.231	-0.808
0.23	1.637	0.18	0.163	-0.802
0.32	1.619	0.12	0.101	-0.728
0.35	1.636	0.10	0.090	-0.765

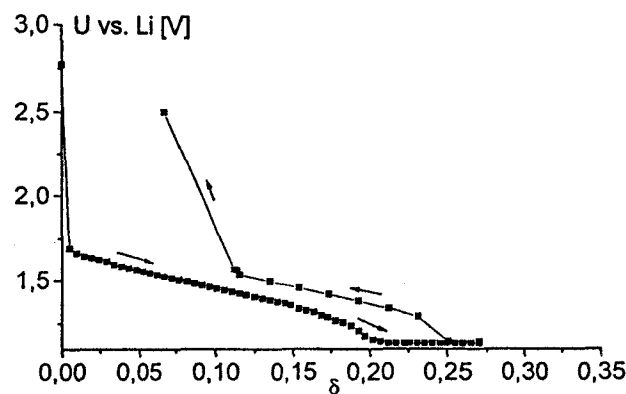


Fig. 3. Coulometric titration curve of $\text{Li}_{0.23+\delta}\text{La}_{0.59}\text{TiO}_3$.

Theoretical calculation showed good agreement with the measured curves if a δ value is taken which is smaller than the maximum structurally available number of A-site vacancies in the specific sample. This can be explained by the fact that non-ideal behaviour due to interactions between the ionic species such as Coulomb repulsion will occur if nearly all available sites are occupied.

Figure 2 shows the fits of the equilibrium potential versus δ for samples of $x = 0.14, 0.23$ and 0.32 and Table 1 gives a summary of the parameters of the fits.

In general, the coulometric titration curves of all samples showed a sharp drop of the potential from 2.8 V vs. lithium (which corresponds to $\delta = 0$) to about 1.7 V vs. lithium (which corresponds to $\delta \approx 1.5 \cdot 10^{-3}$) as the sample starts to become electronically conducting. At the same time, a change in colour from ivory white to grey was observed.

More lithium than expected from the number of available vacancies could be intercalated into some samples without cracking. However, the titration curve was no more s-shaped in this range, but approached a nearly constant value cell voltage, as shown in Fig. 3 for the sample of $x = 0.23$. Possible formation of a second phase at $\delta > 0.18$ may be the reason for this plateau. The intercalated lithium could not be fully extracted from the sample anymore in this case and the sample remained slightly grey after deintercalation.

3.2. Substituted Materials. The main reason for the substitution with transition elements such as Fe, Cr and Mn and rare earth elements such as Pr and Tb is to allow the lithium extraction from the materials by oxidation of the substituted element which forms redox ion pairs. Figure 4 shows the titration curves for the Tb, Pr, Fe and Cr substituted samples.

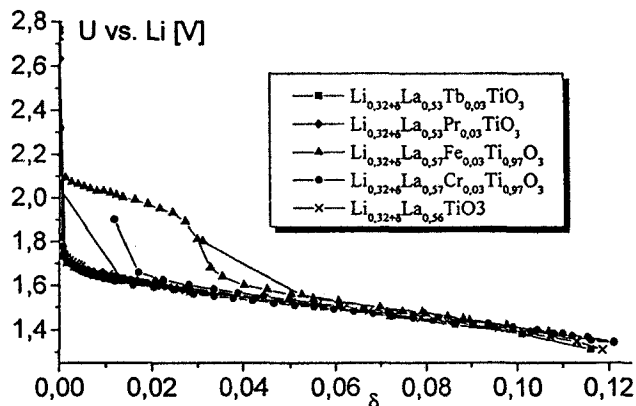


Fig. 4. Coulometric titration of substituted samples.

A different behavior could be observed with the Fe substituted sample. Upon lithium insertion, a reduction of Fe^{3+} to Fe^{2+} occurs at first in the region of about 2.1 V vs. lithium. After about 3 % of lithium were inserted into the material, a rapid drop of the potential follows in the region of about 1.7 V which corresponds to the reduction of Ti^{4+} to Ti^{3+} . Thereafter, the titration curve decreases in the same manner as other substituted and also unsubstituted materials.

Figure 5 shows the titration curves of highly Fe substituted compounds. Since the amount of Fe was increased to 30 %, the shoulder at about 2.1 V extends also to a larger δ -region as compared to the sample with less Fe as shown in the previous figure. On the other hand, since these two materials have smaller numbers of vacancies, δ can not exceed the value of 0.08 or 0.02 for $x = 0.23$ or 0.32, respectively.

As mentioned above, the substitution should allow the extraction of lithium from the materials. However, due to the instability of the employed liquid electrolyte at potentials higher than about 3.5 V, the coulometric titration measurements could only be carried out in the positive δ regime. Nevertheless, polarization measurements [8] at 400 °C by the application of voltages to the highly Fe substituted materials showed that lithium moved from one side of the sample to the other as evidently indicated by the color change of the sample. This process was reversible upon changing the polarity of the applied voltage.

4. Conclusions

The coulometric titration curves can be well described by the theory of randomly disordered solid solutions. The highly Fe substituted materials showed interesting electrical and optical properties in agreement with previous

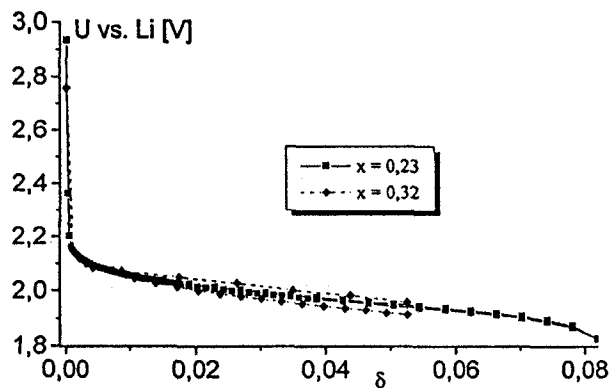


Fig. 5. Coulometric titration of the highly Fe substituted samples.

investigations of the local distribution of the stoichiometry by applying voltages to the materials [8]. For the possible application of the materials in three layer electrochromic devices, further kinetic properties such as chemical diffusion coefficients are currently under investigation.

5. Acknowledgments

The authors wish to thank Thomas Metzger for technical supports.

6. References

- [1] L.L. Kochergina, N.B. Khakhin, N.V. Porotnikov and K.I. Petrov, *Zhurnal Neorganicheskoi Khimii*, **29**, 879 (1984).
- [2] A.G. Belous, G.N. Novitskaya, S.V. Polyanetskaya and Yu.I. Gornikov, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **23**, 470 (1987).
- [3] Y. Inaguma, L. Chen, M. Itoh, T. Nakamura, T. Uchida, H. Ikuta and M. Wakihara, *Solid State Commun.*, **86**, 689 (1993).
- [4] Y. Inaguma, L. Chen, M. Itoh and T. Nakamura *Solid State Ionics*, **70/71**, 196 (1994).
- [5] H. Kawai and J. Kuwano, *J. Electrochem. Soc.* **141**, L78 (1994).
- [6] A.D. Robertson, S. Garcia Martin, A. Coats and A.R. West, *J. Mater. Chem.* **5**, 1405-1412 (1995).
- [7] I.D. Raistrick, A.J. Mark and R.A. Huggins, *Solid State Ionics*, **5**, 351-354 (1981).
- [8] M. Klingler, W.F. Chu and W. Weppner, Paper presented at the 11th International Conference on Solid State Ionics, November 16-21, 1997, Honolulu, Hawaii, USA.