Comments

Comment on A New $La_{2/3}Li_xTi_{1-x}Al_xO_3$ Solid Solution: Structure, Microstructure, and Li^+ Conductivity and A New $La_{2/3-x}Sr_xLi_xTiO_3$ Solid Solution: Structure, Microstructure, and Li^+ Conductivity

In two recent issues of this journal Morata-Orrianta et al. published papers on structure, microstructure, and Li^+ conductivity of two solid solutions $La_{2/3}Li_xTi_{1-x}Al_xO_3$[1] and $La_{2/3-x}Sr_xLi_xTiO_3$.[2] The reader will find in the abstracts (as well as in the text) statements that need some comments. Indeed, the authors wrote in the abstracts of these two papers and in the text as conclusions of their experimental work: "Electrochemical experiments indicate that these materials can be used as electrolytes in secondary batteries having Li metal as the anode down to 1.75 V".

This statement is inconsistent with chemical thermodynamics. Indeed, both electrolytes contain reducible Ti^{4+} ions and therefore cannot be put into contact with Li metal without a redox reaction occurring. This is based on fundamental chemical thermodynamics. If an oxidant with a high redox potential is put into contact with a reductor with a lower redox potential, redox reaction will occur. This is the case with the two redox couples Ti^{4+}/Ti^{3+} (1.75 V/Li) and Li^+/Li (0 V/Li). The difference between the two redox potentials is high enough to produce a fast chemical reaction. Consequently, electrolytes containing Ti^{4+} cannot be used as an electrolyte in secondary batteries in contact with Li metal. This point is generally clearly mentioned in the Introduction of all the papers dealing with these ionic conductor titanates and the authors must not be aware of this scientific point. To overcome this problem, some authors[3] have proposed to intercalate a polymeric membrane between Ti^{4+}-containing electrolyte and Li metal to prevent any chemical reaction. It is worth noting that the authors have shown in both papers that the reduction of Ti^{4+} occurs at 1.75 V/Li for Sr-containing titanate (Figure 8a,b of ref 2) and 1.6 V/Li for Al-containing titanate (Figure 7a,b in ref 1)), which is right, but they wrongly interpreted these results.

The reader may also wonder how to use a battery "down to 1.75 V." This statement has no meaning since as soon as Li is in contact with Ti^{4+} redox reaction will occur and electronic conductivity will appear in the material and short-circuiting of the cell will occur very rapidly.

It can be asked if the partial substitution of titanium by aluminum can prevent the reduction of Ti^{4+} by Li. The answer given by the electrochemical experiments made by the authors is no. The authors obtain good experimental results but they misinterpreted their results.

To summarize, in the two papers of Morata-Orrantia et al., Ti^{4+}-containing oxides have been synthesized but the electrochemical results have been misinterpreted, leading to totally wrong conclusions.

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(1) Morata-Orrantia, A.; Garcia-Martin, S.; Moran, E.; Alario-Franco, M. A. *Chem. Mater.* **2002**, *14*, 2871−2875.

(2) Morata-Orrantia, A.; Garcia-Martin, S.; Moran, E.; Alario-Franco, M. A. *Chem. Mater.* **2003**, *15*, 363−367.

(3) Kobayashi, Y.; Miyashiro, H.; Takeuchi, T.; Shigemura, H.; Balakrishnan, N.; Tabuchi, M.; Kageyama, H.; Iwahori, T. *Solid State Ionics* **2002**, *152/153*, 137−142.

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