



Discussion

Comments on “Li diffusion in $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin film electrodes prepared by pulsed laser deposition” by Xia et al.

Ali Eftekhari*

Department of Chemistry, Ohio Institute of Technology, Cleveland, OH 44101, United States

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In a recent paper [1], Xia et al. have studied Li diffusion inside a typical cathode material of lithium batteries. Although the research strategy is correct, the authors have relied on inappropriate equations for the calculation of diffusion coefficient, which plays a critical role in this study. This is indeed the significant difference in the fundamentals of electrochemistry in electrolyte solution and solid-state electrochemistry. To clarify this problem, voltammetry is typically reviewed here.

It is indeed a common mistake in the electrochemical literature, as equations developed in the electrochemistry textbooks (e.g. [2]) are directly used for solid-state electrochemistry, without considering the essential assumptions. The classical Randles–Sevcik equation

$$I_p = (2.69 \times 10^5) n^{3/2} a D C v^{1/2}$$

has been derived with the following assumptions:

1. Diffusion is one-dimensional from bulk solution towards electrode surface.
2. Electrode surface is ideally smooth.

In lithium battery systems and generally solid-state electrochemistry, diffusion of electroactive species occurs inside the electroactive films. Definitely, there should be diffusion from the bulk solution towards the electrode surface, but this process is quite fast in comparison with the solid-state diffusion; thus, the rate-limiting is the slower process. It is known that electrochemical (voltammetric) behavior of a cathode material in electrolytic cell is almost identical to that in an all-solid-state cell. In the realms of solid-state electrochemistry, solid-state diffusion within the elec-

troactive film predominantly controls the electrochemical system. Thus, when referring to the diffusion coefficient, it is related to the solid-state diffusion, not diffusion inside the electrolyte solution.

On the other hand, diffusion inside the electroactive film is no longer one-dimensional; instead a complicated three-dimensional diffusion towards accessible active sites for insertion/extraction process.

If assuming that the electroactive film is extremely thin (e.g. monolayer) as the insertion/extraction process is mainly occurs at the film surface; the classic Randles–Sevcik equation is still invalid. As stated before, the classic Randles–Sevcik equation is based on an assumption that the electrode surface is entirely smooth; however, electroactive films like metal oxides are known to have significantly rough surfaces. For rough surfaces, the classic Randles–Sevcik should be modified as a new parameter replaces the power of scan rate [3]. In the case of a smooth two-dimensional surface, it equals to 1/2 to form the classic Randles–Sevcik, but not for a case like cathodes of lithium batteries.

Another common mistake in using Randles–Sevcik equation is to ignore that the active electrode area is indeed the real surface area, not geometrical area. In an ideal case of oxidation/reduction reaction at gold surface, this means that roughening the electrode surface (i.e. increasing the real surface area) increases the diffusion coefficient, since a (if assuming to be the geometrical electrode area) remains unchanged.

In general, Randles–Sevcik and similar equations, which have been developed for diffusion towards electrode surfaces, are not valid for electrochemistry of electroactive films. Although there is a single electrochemical cell, the processes occur in quite different media.

References

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* Tel.: +1 216 539 0610; fax: +1 216 539 2000.

E-mail address: eftekhari@elchem.org.