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Corresponding Author: Prof John Robert Owen, PhD

Corresponding Author's Institution: University of Southampton

First Author: John R Owen, PhD

Order of Authors: John R Owen, PhD; Phil A Johns, M.Chem; Matthew R Roberts, M.Chem; Yasuaki Wakizaka, PhD; James H S, M.Chem

Abstract: Examples of LiFePO₄ composite electrodes are shown in which solid state and interfacial processes are not the principal rate limiting process during fast discharge. Rate dependence on electrode thickness, electrolyte concentration, lithium transference number, and dilution of the active material is explained by a simple salt diffusion model. A discharge to 25 % capacity (0.3 mA h) was obtained on a 40 micrometre thick electrode after only 4 s in an optimised electrolyte - aqueous Li₂SO₄.



**University
of Southampton**

School of Chemistry

Professor John Owen

University of Southampton
Highfield
Southampton
SO17 1BJ United Kingdom

Telephones:
Direct line +44 (0)23 8059 2184
Fax +44 (0)23 8059 3781
Email jro@soton.ac.uk

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Dear Professor Belanger,

How the electrolyte limits fast discharge in nanostructured batteries and supercapacitors
Phil A. Johns, Matthew R. Roberts, Yasuaki Wakizaka¹, James H. Sanders and John R. Owen*
School of Chemistry, University of Southampton, SO17 1BJ

I confirm that this article is original, unpublished, and not being considered for publication elsewhere

I would like to suggest the following reviewers:

Prof. M.B. Armand
michel.armand@u-picardie.fr

Prof. J. Dahn
jeff.dahn@dal.ca

Dr P. Nelson
phil_nelson2@hotmail.com

Prof. A.V. Chadwick
A.V.Chadwick@kent.ac.uk

Prof. M. Stanley Whittingham
stanwhit@binghamton.edu

Yours Sincerely,

John Owen

¹ Now at Showa Denko K.K , 1-1-1, Ohnodai, Midori-ku, Chiba-Shi, Chiba, 267-0056 Japan.

Dear Prof. Belanger

Electrolyte limitation of fast discharge in lithium batteries and supercapacitors

Phil A. Johns, Matthew R. Roberts, Yasuaki Wakizaka¹, James H. Sanders and John R. Owen*
School of Chemistry, University of Southampton, SO17 1BJ

Publication of this paper is extremely urgent because it provides an alternative model with evidence for an alternative explanation for the recent results in a published in Nature by Kang and Ceder, concerning ultra-fast discharge of LiFePO₄. Several prominent workers in the field, including Ceder, are aware of the work described in the present manuscript because I gave an outline of it at recent conferences. However, the significance of the work was not fully appreciated until the Kang paper came out in March. Since then I have received countless messages asking where I published the model so they can reference the work. Of course, I have had to reply “coming asap!”.

Yours sincerely,

John Owen

¹ Now at Showa Denko K.K., 1-1-1, Ohnodai, Midori-ku, Chiba-Shi, Chiba, 267-0056 Japan.

Suggested Reviewers

Prof. M.B. Armand
michel.armand@u-picardie.fr

Prof. J. Dahn
jeff.dahn@dal.ca

Dr P. Nelson
phil_nelson2@hotmail.com

Prof. A.V. Chadwick
A.V.Chadwick@kent.ac.uk

Prof M. Stanley Whittingham
stanwhit@binghamton.edu

How the electrolyte limits fast discharge in nanostructured batteries and supercapacitors

Phil A. Johns, Matthew R. Roberts, Yasuaki Wakizaka¹, James H. Sanders and John R. Owen*

School of Chemistry, University of Southampton, SO17 1BJ

**jro@soton.ac.uk*

Abstract

Examples of LiFePO_4 composite electrodes are shown in which solid state and interfacial processes are not the principal rate limiting process during fast discharge. Rate dependence on electrode thickness, electrolyte concentration, lithium transference number, and dilution of the active material is explained by a simple salt diffusion model. A discharge to 25 % capacity (0.3 mAh) was obtained on a 40 μm thick electrode after only 4 s in an optimised electrolyte - aqueous Li_2SO_4 .

Keywords lithium ion battery, LiFePO_4 , discharge rate, electrolyte, composite electrode, transference

1. Introduction

One of the greatest benefits of nanostructured electrodes [1-4] is maximisation of the interfacial area between the electrode and electrolyte, minimisation of the solid state diffusion distance L ; both of these should improve the discharge rate according to L^{-2} if interfacial or solid state transport processes are the limiting factors. However, recent work in our laboratory with nanostructured electrodes for lithium ion batteries have shown disappointing results compared to the sub-second discharges [1] previously seen in thin nickel oxyhydroxide electrodes with aqueous KOH. This paper describes how we have overcome this problem in the LiFePO_4 electrode, not by addressing the solid nanostructures, but the dimensions and composition of the entire electrode, including the electrolyte occupying the void space due to porosity.

LiFePO_4 , is a popular active material in the lithium ion positive electrode because of its low cost, cyclability, modest energy density, and safety [5]. Slow discharge rates were obtained initially because of its low electronic conductivity, which resists inter-particle and intra-particle electron transport. Electron transfer between particles and the electronic conduction network has recently improved with carbon coating [6-9] ; long range electron and ion transport have been improved by careful control of the composition and structure

¹ Now at Showa Denko K.K , 1-1-1, Ohnodai, Midori-ku, Chiba-Shi, Chiba, 267-0056 Japan.

of the composite electrode [10] which supports the active material with carbon black and a binder, leaving some open porosity for admission of some electrolyte. Concerning electron transport within the particles themselves, enormous enhancements in conductivity and consequent rate improvements has been claimed as a result of adding dopants to the structure[11]. However, other studies showing much more modest enhancements [12, 13] bring into question whether the real cause may have been a change in particle morphology, agglomeration, or electrode porosity as a result of introducing the impurity. Another study suggests that phase nucleation co-located with ion and electron injection may be more important than solid state diffusion in this material[14].

Gaberscek *et al* have suggested that a high rate capability in a composite electrode is also strongly dependent on the resistance of the ionic and electronic “wiring” [15] and therefore responds to a decrease in the electrode thickness.

The present work suggests a third effect - salt diffusion in the composite electrode matrix – may be an important factor in high rate discharge. The lithium ion transference number, T_{Li+} defines the number of moles of lithium species transported into the cathode by *migration* alone during the passage of one Faraday of charge. Its complement $(1-T_{Li+})$ or T_- defines the number of moles of lithium that cannot take part in the electrode reaction until they have reached the active particle surfaces by *diffusion*. The aim of this work is to assess the significance of restricted lithium salt diffusion in the nanocomposite battery electrode, as compared with solid state ion transport effects that have recently drawn much attention from the press with reports of ultra-fast discharge rates[16] that are supposed to be due to enhanced solid state transport in nanomaterials.

$LiFePO_4$, has a flat discharge curve, due to the co-existence of two phases during discharge. Our model assumes that each electrode particle is either fully charged or discharged, interfacial and solid state

restrictions are absent, and therefore the electrolyte resistance is the only restriction, at least initially. Current should then flow into the particles nearest the separator until they are completely discharged. Subsequently a layer of discharged material should proceed deeper into the electrode, while the potential drop to the nearest undischarged material increases, producing a linear galvanostatic discharge profile as in Fig. 1(a).

In reality, discharge curves of FePO_4 do not resemble Fig. 1(a). Following a small increase in the IR drop, the criterion for discharge is a precipitously steep decline in potential as shown in Fig. 1(b). The “shrinking core” [17] and other solid state models [14] explain this by saturation of the $\text{Li}_{1-x}\text{FePO}_4$ phase at the electrode/electrolyte interface. We explain the phenomenon by a lithium salt deficiency due to a non-unity transference number according to the Sharp Discharge Front (SDF) model shown in Fig. 1(c).

Fig. 1 here

2. The Sharp Discharge Front Model

The SDF model incorporates the transference number T_+ in a similar way to the simulations of West *et al.* [18] then Fuller, Doyle and Newman [19] with the following approximations.

- A sharp planar boundary between discharged and charged material perpendicular to the current direction.
- A negligible initial concentration of lithium salt LiX in the composite compared with the total demand for lithium during discharge.
- Constant $[\text{LiX}]$ in the separator.
- Constant values of the diffusion coefficient D_{LiX} and transference numbers.

The diffusion equations are as follows:

$$J_{\text{LiX}} = \left(\frac{jT_-}{F} \right) = -D_{\text{LiX}} \left(\frac{d[\text{LiX}]}{dx} \right) \quad (1)$$

$$[LiX] = [LiX]_0 + \lambda \left(\frac{d[LiX]}{dx} \right)$$

where λ is the thickness of discharged material

(2)

A premature end of discharge occurs when $[LiX] \rightarrow 0$ and $\lambda = \lambda_{\max}$:

$$\lambda_{\max} = - \frac{[LiX]_0}{\left(\frac{d[LiX]}{dx} \right)} = \frac{FD[LiX]_0}{(T_-)j}$$

(3)

The degree of discharge, DoD as a function of the current density j is as follows:

$$DoD = \frac{\text{charge}}{\text{theoretical charge}} = \frac{\lambda_{\max}}{L} = \frac{FD[LiX]_0}{(T_-)jL}$$

(4)

where,

$$j = f \cdot Q_A^0 = f \cdot Q_V^0 L = f \cdot [Li] FL$$

(5)

and Q_A^0 , Q_V^0 are the theoretical charge per unit area and volume respectively and $[Li]$ is the molar demand for lithium in the charged active material per unit volume of composite.

Finally

$$DoD \cdot f = \frac{D}{L^2} \frac{[LiX]_0}{(T_-)[Li]}$$

(6)

3. Experimental

Composite electrode construction. Pellets containing mixtures of LiFePO_4 (Aldrich 99.5+% carbon coated, battery grade, thin platelets $\sim 2\text{-}5\ \mu\text{m}$ across), TiO_2 (Aldrich nanopowder, 99.7%, anatase) acetylene black (Shawinigan Black 100% compressed, Chevron Philips chemical company) and poly tetrafluoroethylene PTFE powder (type 6C-N, DuPont) were made into composite electrode pellets with varying percentages of LiFePO_4 . The percentage of LiFePO_4 was varied from 1 to 99% (1,2,5,10,20,50,80,95,97 and 99% LiFePO_4) with the percentage of TiO_2 being varied such that the percentage of acetylene black and PTFE remained constant (20 and 5% respectively). The LiFePO_4 was mixed with the TiO_2 , acetylene black and PTFE binder (or PVdF in cyclopentanone for the experiment with an ionic liquid electrolyte), using a pestle and mortar to produce a crude film, this was mechanically rolled to produce an even film of desired thickness (average thickness $70\ \mu\text{m}$) from which electrode pellets (0.95cm^2) were produced and dried at 120°C .

Cell assembly. Two electrode cells were constructed using metallic lithium as both counter and reference electrode, 1M LiPF_6 in ethylene carbonate/dimethyl carbonate (EC/DMC) 1:1 by weight (LP30, Merck) soaked in two glass fibre separators ($\sim 50\ \mu\text{m}$ each, GF/F, Whatman) was used as the electrolyte. The electrodes/ electrolyte were compressed within a spring loaded stainless steel cell such that the final assembly consisted of; stainless steel lid/current collector | metallic lithium counter and reference | Glass fibre separators soaked in 1M LiPF_6 in EC/DMC | LiFePO_4 , TiO_2 composite pellet | aluminium current collector | spring | Stainless steel base (sealed using a Viton rubber O-ring). For the ionic liquid cell the same construction was used except the electrolyte was 1M LiTFSI in EMI TFSI. For the aqueous cell, the pellet was pressed onto platinum gauze and suspended in the 1 M Li_2SO_4 electrolyte, which contained a carbon felt counter electrode and SCE as the reference.

Galvanostatic cycling. Cells were cycled galvanostatically (using a 16-channel VMP2, Princeton Applied Research; Biologic-Science Instruments) between 4.5 and 1.2 V vs. Lithium at a variety of current densities

with a 1 hour potentiostatic equilibration at the potential limits. The DoD was defined by reference to the maximum charge obtained during a discharge at C/7 (140 mA h g⁻¹).

4. Results and Discussion

Fig. 2 shows a dramatic decrease in DoD with electrode thickness at 10 C for the standard electrolyte EC:DMC. In the region below 30 % DoD the gradient is approximately -2, corresponding to the theory. The restrictions at higher DoD values can be attributed to large electrode particles, the associated interfacial and diffusional overpotentials. Also shown is the effect of changing the electrolyte – first to the ionic liquid EMI TFSI giving a lower DoD at the same rate, and then to water giving a much higher rate - 900 C in 1M Li₂SO₄. These results are consistent with an ionic liquid diffusion coefficient one order of magnitude lower, and an aqueous diffusion coefficient two orders higher, than that of the standard electrolyte.

Fig. 2. here

Fig. 3 shows that the rate for a given DoD depends on the dilution of the electrode material with a three-fold increase in the gradient of the plot below 50 % DoD in Fig 4(c) for the diluted electrode. At higher DoD values, the gradient decreases because the discharge includes large particles or agglomerates, where solid state diffusion and interfacial processes could well be limiting factors.

Fig. 3 here

Taking a T_+ value of 0.3[20], equation (6) applied to the 80 % LiFePO₄ line of Fig. 3(c) gives a value of $D \sim 10^{-11} \text{ m}^2 \text{ s}^{-1}$ which can be considered reasonable given the low porosity and high tortuosity of the electrolyte path within the composite. A recent literature value for the same electrolyte[20] shows D to be between 2 and $4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ over the concentration range 1M to zero.

An interesting feature of the results is that the electrolyte diffusion restriction applies only at the higher rates, and low DoD. This region represents the discharge of small particles in which the solid state processes are fast. DoD restrictions above 50% , showed lower rates than predicted by the model; however these were not very sensitive to the nature of the electrolyte, composite thickness, nor active material dilution and therefore can be attributed to the discharge of larger particles, whose diffusion time constants exceed those of electrolyte diffusion through the composite network. This illustrates the general point that for a given electrode material there is an optimum particle size, below which further decrease is hardly productive because of the liquid diffusion restriction in the composite. We believe that in LiFePO_4 this is of the order of 500 nm radius – the dimension of most of the particles in our samples.

In conclusion, we state that the salt depletion model has been shown to apply in the fast discharge rate regime, as illustrated by the result of a 4-second discharge to 25 % capacity (0.3 mAh , 20 mA cm^{-3}) with a $40 \text{ }\mu\text{m}$ electrode in a $1\text{M Li}_2\text{SO}_4$ aqueous electrolyte. As indicated in the title, the results may be more relevant to redox supercapacitors than batteries.

6. Acknowledgement

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d. Figure(s)

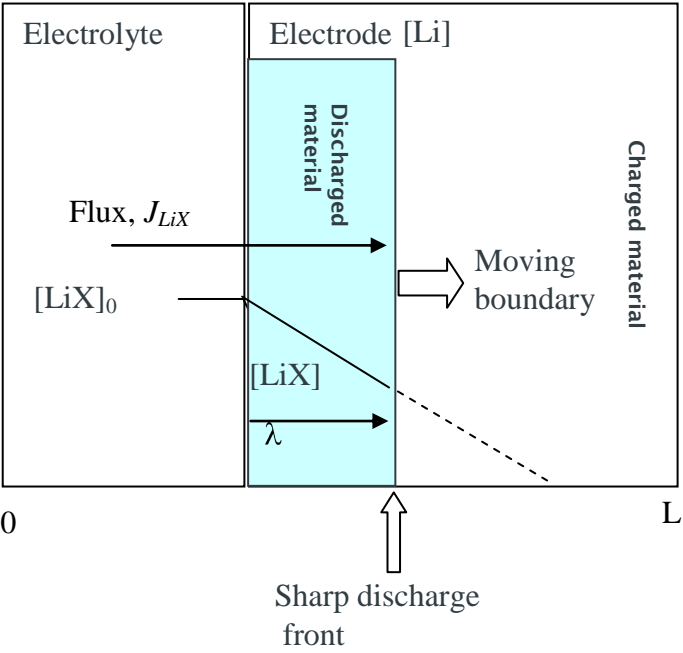
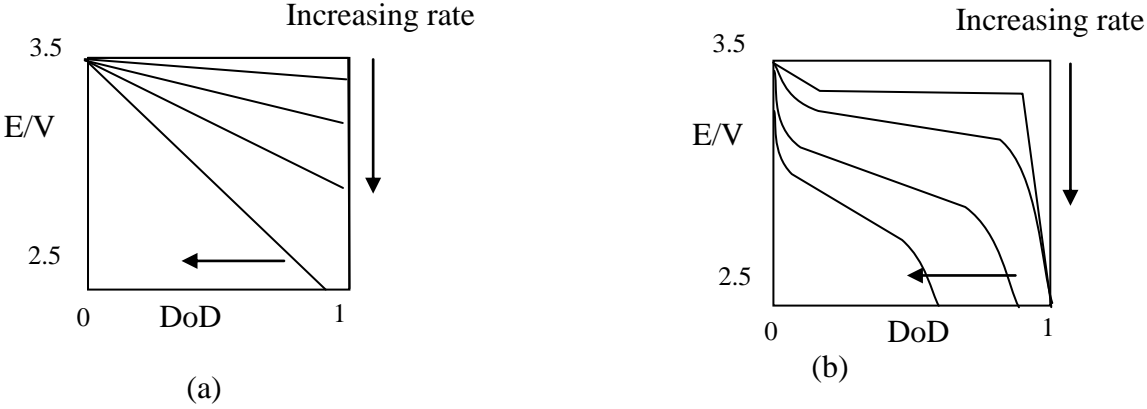


Figure 1

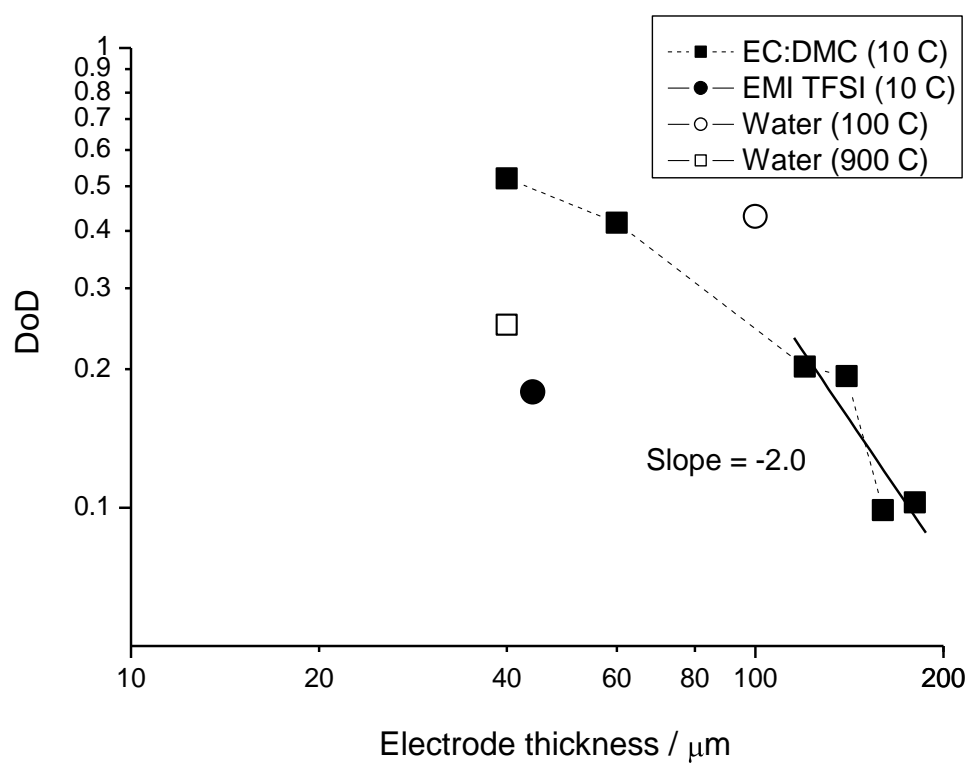
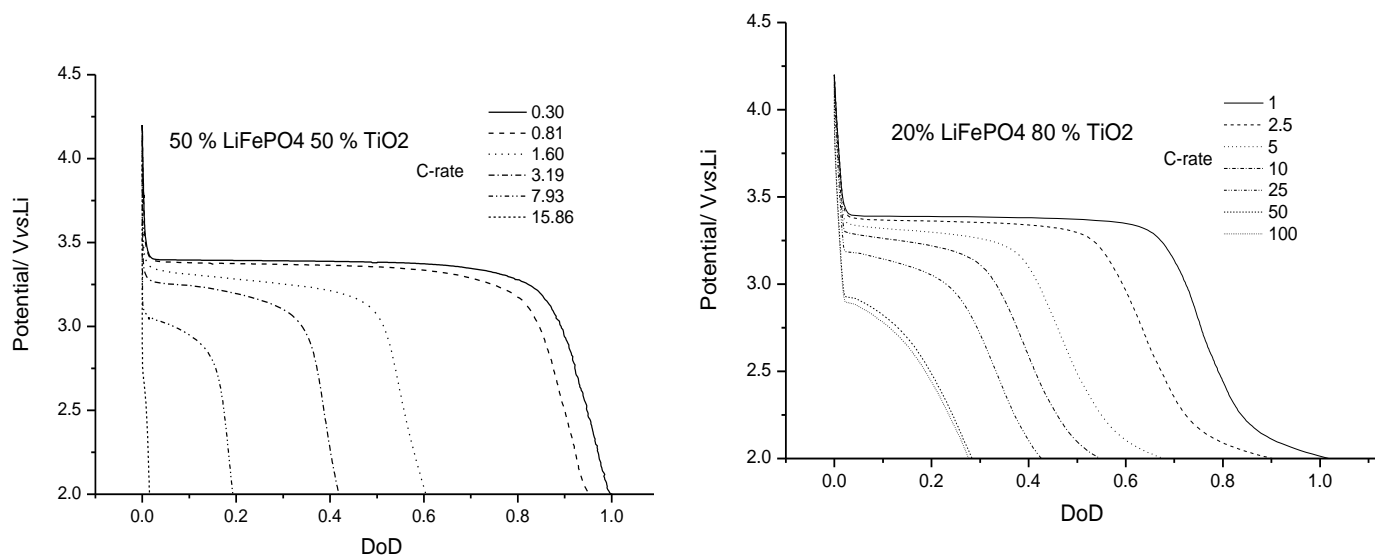


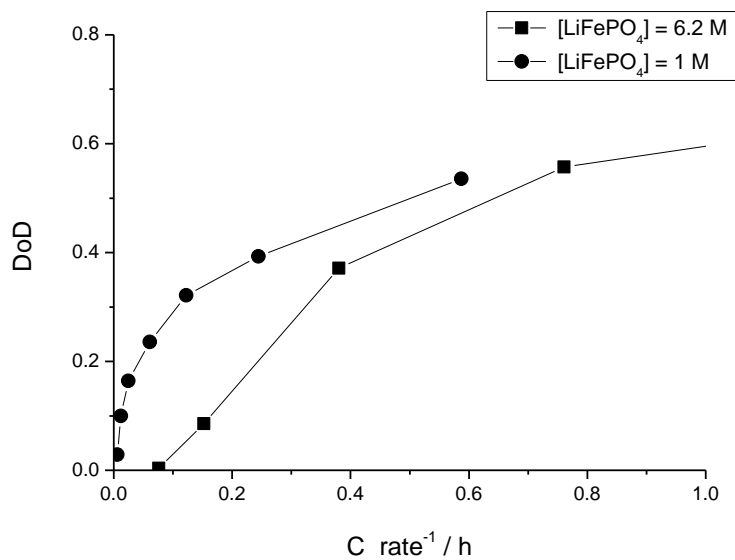
Figure 2 Owen

d. Figure(s)



(a)

(b)



(c)

Figure 3 Owen