Recent atomistic modelling studies of energy materials: batteries included

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Advances in functional materials for energy conversion and storage technologies are crucial in addressing the global challenge of green sustainable energy. This article aims to demonstrate the valuable role that modern modelling techniques now play in providing deeper fundamental insight into novel materials for rechargeable lithium batteries and solid oxide fuel cells. Recent work is illustrated by studies on important topical materials encompassing transition-metal phosphates and silicates for lithium battery electrodes, and apatite-type silicates for fuel cell electrolytes.

Keywords: modelling; fuel cell; lithium battery; olivine-phosphate; apatite

1. Introduction

A major worldwide challenge is unquestionably the development of cleaner, sustainable supplies of energy to deal with the environmental threat of global warming and the finite nature of fossil fuels. However, there is no one universal solution. A variety of energy conversion and storage technologies are being developed to help cut carbon emissions. The performance of these energy systems, which include lithium batteries and fuel cells, depends crucially on the properties of their component materials. Indeed, innovative materials science lies at the centre of advances that have already been made in this field.

This article addresses new materials for two important clean energy technologies: first, rechargeable lithium batteries, which are essential to meet the requirements of future portable consumer equipment and hybrid electric vehicles (Tarascon & Armand 2001; Whittingham 2004; Arico et al. 2005; Armand & Tarascon 2008; Bruce 2008), and, second, solid oxide fuel cells (SOFCs), which are suitable for combined heat and power generation in homes and other stationary applications (Kilner 2000; Brett et al. 2008; Orera & Slater 2010).

For the next generation of energy devices, the discovery and optimization of new materials are critical to future breakthroughs. This depends on exploring new classes of compounds and a better understanding of the fundamental science of functional materials. However, an atomic-scale understanding of the structure–property relationships in new complex systems is often lacking.

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Computer modelling techniques are now well-established tools in the field of materials chemistry research, and have been applied successfully to studies of structures and dynamics of solids on the atomic and nano-scale. A major theme of the modelling work has been the strong interaction with experimental studies. Although numerous examples of the studies of others will be mentioned, it is beyond the scope of this article to give an exhaustive review of all the excellent work in this active research field. Rather, this article focuses on important topical materials to show recent progress in computational research on electrode materials for lithium batteries (such as iron phosphate) and on ion conductors for SOFCs (such as apatite silicates).

2. Materials modelling methods

In general, three main classes of technique have been employed in the study of solid-state ionic materials: atomistic (static lattice), molecular dynamics (MD) and quantum mechanical (QM) \textit{(ab initio)} methods; our description of these techniques will be brief since comprehensive reviews are given elsewhere (Smith & Forester 1994; Catlow 1997; Gale 1997; Koch & Holthausen 2001).

First, atomistic simulation methods determine the lowest energy configuration of the crystal structure by employing efficient energy minimization procedures. The calculations rest upon the specification of an interatomic potential model, which expresses the total energy of the system as a function of the nuclear coordinates. For solid-state ionics, the Born model framework is commonly employed, which partitions the total energy into long-range Coulombic interactions and a short-range term to model the repulsions and van der Waals forces between electron charge clouds. The shell model provides a simple description of polarizibility effects and has proved to be effective in simulating dielectric and lattice dynamical properties. It should be stressed, as argued previously (Catlow 1997), that employing such a potential model does not necessarily mean that the electron distribution corresponds to a fully ionic system, and that the general validity of the model is assessed primarily by its ability to reproduce the observed properties of the crystal lattice, such as unit cell parameters.

An important feature of these calculations is the treatment of lattice relaxation (using the Mott–Littleton approach) around the point defect, dopant cluster or migrating ion, so the crystal is not considered simply as a rigid lattice. These methods are embodied in the GULP simulation code (Gale 1997). The atomistic modelling of surface structures and energies uses a similar methodology to bulk calculations, describing the crystal as a stack of planes periodic in two dimensions.

The second main type of simulation method is the molecular dynamics (MD) technique, which consists of an explicit dynamical simulation of the ensemble of particles for which Newton’s equations of motion are solved numerically. As before, classical interatomic potentials are also used to treat the forces, with repetition of the integration algorithm yielding a detailed picture of the evolution of ion positions and velocities as a function of time. A widely used MD code is the DL\_POLY program (Smith & Forester 1994).
Finally, we note that there is an expanding role for QM or \textit{ab initio} methods to provide information on the electronic structure of the solid. Techniques based on density functional theory (DFT) are now increasingly viewed as an important approach in materials science with the exchange-correlation energy being treated by the local density approximation or the generalized gradient approximation (incorporated in the VASP (Kresse & Furthmüller 1996) and CASTEP packages (Payne \textit{et al.} 1992)). There is also the use of hybrid exchange functionals (such as B3LYP) within the DFT. A widely used implementation of DFT combines a plane-wave basis set with the ‘pseudopotential’ method in which the pseudopotential replaces the core electrons by an effective potential in which the valence electron states can evolve. More recently, there is the use of DFT+U for open-shell transition-metal compounds, where $U$ is the on-site Coulomb interaction parameter.

3. Cathode materials for lithium batteries

The rechargeable lithium ion battery consists of a positive electrode (generally the lithium metal oxide, LiCoO$_2$) and a negative electrode (generally graphite), these being separated by a lithium ion-conducting non-aqueous liquid electrolyte. In this field of lithium battery research, there is tremendous activity devoted to finding alternatives to cobalt oxide electrodes, particularly for potential use in hybrid electric or pure electric vehicles to help reduce CO$_2$ emissions from road transport (Tarascon & Armand 2001; Whittingham 2004; Arico \textit{et al.} 2005; Armand & Tarascon 2008; Bruce 2008). The Co-based materials pose problems for such large-scale automotive applications, largely associated with cost and environmental hazard. Current candidates include Mn- or Fe-based materials such as layered oxides (e.g. LiNi$_{0.5}$Mn$_{0.5}$O$_2$), spinel oxides (e.g. LiMn$_{1.5}$Ni$_{0.5}$O$_4$) and polyanionic materials (e.g. LiFePO$_4$, Li$_2$MnSiO$_4$). To highlight recent trends in modelling work in this area, we focus on the topical Fe phosphate system and the novel Mn silicate material.

\textit{(a) LiFePO$_4$: surfaces and morphology}

The olivine-structured orthophosphate LiFePO$_4$ has become a highly promising cathode material for use in lithium ion batteries because of its electrochemical performance (high operating voltage, large theoretical gravimetric capacity), as well as its low cost and safety advantages (Padhi \textit{et al.} 1997; Ravet \textit{et al.} 2001; Chung \textit{et al.} 2002; Subramanya Herle \textit{et al.} 2004; Delacourt \textit{et al.} 2005; Chen \textit{et al.} 2008; Muraliganth \textit{et al.} 2008; Hamelet \textit{et al.} 2009; Kang & Ceder 2009; Ramana \textit{et al.} 2009; Saravanan \textit{et al.} 2009). The LiFePO$_4$ olivine structure (figure 1) consists of PO$_4$ tetrahedra with Fe$^{2+}$ ions on corner-sharing octahedral positions and Li$^+$ ions on edge-sharing octahedral positions, the latter running parallel to the $b$-axis.

After simulating the observed orthorhombic structure, atomistic simulation studies (Islam \textit{et al.} 2005) suggest that the most favourable intrinsic defect in bulk LiFePO$_4$ is the ‘anti-site’ defect, for which a small population (less than 2\%) of Li$^+$ and Fe$^{2+}$ ions is expected to exchange sites (which we also find for other olivines.}

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LiMPO$_4$ (M = Mn, Co, Ni) (Fisher et al. 2008; Gardiner & Islam 2010); this defect would be temperature dependent and hence sensitive to experimental synthesis conditions. Structural analysis of hydrothermally synthesized LiFePO$_4$ suggests 3 mol% Fe on the lithium sites (Ramana et al. 2009; Saravanan et al. 2009) while a recently reported scanning transmission electron microscopy study (Chung et al. 2008) has observed anti-site defects in LiFePO$_4$, quoting a concentration of around 1 per cent. In the mineralogy field, this type of anti-site defect or ‘intersite exchange’ has been discussed in relation to olivine silicates such as MgFeSiO$_4$ and MnFeSiO$_4$ (Henderson et al. 1996).

The formation of LiFePO$_4$ particles of submicron or nano-metre size is thought to enhance electrochemical performance by reducing transport path lengths, as well as being important for the electrode/electrolyte interface (Whittingham 2004; Arico et al. 2005; Ellis et al. 2007). It is also clear that morphological control of nano-crystalline materials is becoming increasingly important.

Given the significance of surface structure and (nano)particle morphology on the properties of LiFePO$_4$, knowledge of these features on the atomic level would provide valuable information for understanding electrochemical mechanisms. The variety of synthesis techniques, however, makes it difficult to extract such fundamental detail or identify distinct surface planes by experiment alone.

As with bulk simulations, advanced atomistic methods can be used to examine surface structures and crystal morphologies. First, relaxed surface structures and energies were calculated for 19 low-index planes of LiFePO$_4$ (Fisher & Islam 2008). The surface structures exhibit a complex, uneven topology on account of the different sizes of the three constituent moieties, Li$^+$, Fe$^{2+}$ and PO$_4^{3−}$. The majority of the surfaces undergo considerable relaxation, which confirms that the surface chemistry and electrochemical activity cannot be reliably predicted by assuming rigid, unrelaxed terminations of the bulk lattice.
Almost all of the low-energy surfaces are lithium-deficient relative to the bulk lattice, requiring Li vacancies at the surface; this may become increasingly important for Li intercalation with the decreasing size of the crystalline particles. The calculated growth morphology (shown in figure 2) is terminated by \{010\}, \{100\} and \{101\} faces, which are expected to play a significant role in the electrochemical properties of the material. The crystal shape is anisotropic, with an elongated hexagonal prism-like shape capped by \{010\} faces; this morphology is consistent with some SEM images of pure LiFePO$_4$ (Franger et al. 2005), although different synthesis routes have produced a variety of crystallite morphologies (Chen et al. 2006; Ellis et al. 2007) such as hexagonal platelets and block-type shapes.

The exposure of the (010) surface is significant since it is normal to the most facile pathway for lithium ion conduction (along the [010] channel), and hence important for the reversible insertion/de-insertion of lithium ions (shown in figure 3). The (010) surface may also be important in relation to studies of the LiFePO$_4$/FePO$_4$ boundary interface.

SEM images of plate-like crystallites of uncoated LiFePO$_4$ from hydrothermal synthesis exhibiting large (010) faces (Chen et al. 2006) have been reproduced by our methods for direct comparison (shown in figure 4). This reduction in the diffusion path length of lithium ions is expected to enhance the electrochemical performance of a cathode prepared from such a material.

(b) $\text{Li}_2\text{MnSiO}_4$: lithium ion mobility

Recently, the orthosilicate family including Li$_2$FeSiO$_4$ and Li$_2$MnSiO$_4$ has been found to show good electrochemical performance as potential cathode materials for lithium batteries (Arroyo-de Dompablo et al. 2006, 2008; Dominko et al. 2006, 2009; Gong et al. 2006; Nyten et al. 2006; Zaghib et al. 2006; Kokalj et al. 2007; Lyness et al. 2007; Politaevev et al. 2007; Nishimura et al. 2008a; Ghosh et al. 2009). A key feature of Li$_2$FeSiO$_4$ and Li$_2$MnSiO$_4$ is that, in principle, extraction...
of two lithiums is possible (for a two-electron redox process); this should produce a higher capacity than the olivine phosphates in which one lithium at most can be extracted. In addition, it may be possible to remove more than one lithium more readily from Li$_2$MnSiO$_4$ than from Li$_2$FeSiO$_4$, since the higher manganese oxidation state Mn$^{4+}$ is far more accessible than Fe$^{4+}$.

There has been significant debate concerning the observed structures of Li$_2$MnSiO$_4$, with two structures being proposed: orthorhombic (space group $Pmn2_1$), based on $\beta$-Li$_3$PO$_4$ (Dominko et al. 2006), and monoclinic (space
group $P2_1/n$), based on $\gamma$-Li$_3$PO$_4$ (Politaev et al. 2007). Both monoclinic and orthorhombic Li$_2$MnSiO$_4$ polymorphs are based on a distorted hexagonal close-packed array of oxygen ions with all cations in corner-sharing tetrahedra, but differ in the orientation of these tetrahedra, particularly for the MnO$_4$–SiO$_4$ chains (shown in figure 5).

The intrinsic lithium ion mobility in and out of the Li$_2$MnSiO$_4$ material is of crucial importance when assessing its use as a possible high-rate cathode material in lithium batteries. However, the diffusion paths in the Li$_2$MnSiO$_4$ polymorphs have not been clearly established. Using atomistic simulation techniques, it is possible to examine various possible diffusion paths responsible for lithium ion conduction, which are often difficult to probe on the atomic scale by experiment alone.

Recent simulation results (Kuganathan & Islam 2009) indicate that the lowest activation energies for Li migration in the monoclinic and orthorhombic structures are 0.54 and 0.95 eV respectively. Such significant differences in intrinsic Li mobility would influence the ability to extract lithium from the two polymorphs, and hence lead to contrasting rate capability and capacity retention as rechargeable electrodes. A related feature is the possible coexistence of the two structural polymorphs in the as-prepared Li$_2$MnSiO$_4$.

The results also show curved conduction paths and anisotropic Li transport (shown in figure 5), which are probably general for the Li$_2$MSiO$_4$ ($M = \text{Mn, Fe, Co}$) orthosilicate family of compounds. Although there are no Li ion conductivity data for this system for direct comparison, the calculated value of about 0.5–0.6 eV for the monoclinic polymorph is consistent with experimental activation energies in other framework-structured or LISICON-type materials (Sebastion & Gopalakrishnan 2003).

It is recognized that there is still debate concerning the observed structures of the Li$_2$MnSiO$_4$ material either as-prepared or upon cycling; in any case, these new silicate-based lithium battery materials warrant further investigation.

4. Materials for solid oxide fuel cells (SOFCs): apatite ion conductors

There is considerable interest in SOFCs owing to their high efficiency and ability to act as a bridging technology between hydrocarbon and hydrogen fuel systems (Kilner 2000; Brett et al. 2008; Orera & Slater 2010). The SOFC is an electrochemical power generation device that relies on the transport of oxide ions or protons across a ceramic oxide membrane.

There is significant activity in developing alternative ion conductors to the conventional Y/ZrO$_2$ electrolyte to operate at lower temperatures (500–700°C) for the so-called intermediate-temperature SOFCs. To date, oxide materials exhibiting the fluorite or perovskite structures have dominated research on electrolytes for SOFCs (Kilner 2000; Brett et al. 2008; Orera & Slater 2010). Recently, however, a range of rare-earth apatite materials have been proposed as alternative solid electrolyte materials following the exciting discovery of fast oxide ion conductivity in these silicate systems (Sansom et al. 2001; León-Reina et al. 2004, 2007; Najib et al. 2004; Nakayama et al. 2004; Kendrick et al. 2007a; Panteix et al. 2008; Yoshioka et al. 2008).

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Figure 5. Crystal structures of Li$_2$MnSiO$_4$ showing the lowest energy paths for lithium ion migration: (a) monoclinic structure; (b) orthorhombic structure. Blue spheres are Li ions; yellow and green tetrahedra are SiO$_4$ and MnO$_4$, respectively.

Figure 6. Structure of the apatite–silicate La$_{10-x}$Si$_6$O$_{26}$, showing SiO$_4$ tetrahedra (blue), La ions (green) and channel oxygens (red).

Isostructural with the well-known mineral hydroxyapatite (related to that found in bones and teeth), the silicate-based materials have the general formula Me$_{10}$(SiO$_4$)$_6$O$_{2+y}$, where Me is a metal such as a rare earth or alkaline earth. The crystal structure (shown in figure 6) comprises isolated SiO$_4$ tetrahedra arranged so as to form two distinct channels running parallel to the c-axis. Occupying the smaller of these channels are Me cations, while the larger channel contains oxide ions.

Early experimental work indicated the importance of interstitial oxide ions (Sansom et al. 2001; Leon-Reina et al. 2004, 2007; Najib et al. 2004; Kendrick et al. 2007). In order to investigate the defect chemistry and conduction mechanism in more detail, atomistic modelling studies (Tolchard et al. 2003) were performed.

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for the first time on the two systems: $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ and $\text{La}_8\text{Sr}_2(\text{SiO}_4)_6\text{O}_2$; the former showing high conductivity while the latter is a poor oxide ion conductor.

A principal result of this work was that the interstitial oxygen, rather than being located down the channel centre as initially thought, was accommodated at the channel periphery. This position is stabilized by the displacement of the nearby silicate unit towards the La channels, accounting for the high thermal displacement parameters observed for the silicate oxygen atoms. Subsequently, the predicted location of this channel periphery site was confirmed by neutron diffraction studies (Leon-Reina et al. 2004, 2007; Kendrick et al. 2007a).

Additional support for this interstitial oxide ion site has come from $^{29}\text{Si}$ NMR studies of a range of alkaline earth-doped apatite silicates (Sansom et al. 2006). These studies have shown a correlation between the $^{29}\text{Si}$ NMR spectra and the conductivity, with poorly conducting samples demonstrating a single NMR resonance, whereas in fast ion-conducting compositions an extra peak was apparent, attributed to a silicate group adjacent to an interstitial oxygen site.

In terms of oxide ion mobility, the simulation results suggested that the conduction mechanism in $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ is via an interstitial mechanism, while that of $\text{La}_8\text{Sr}_2(\text{SiO}_4)_6\text{O}_2$ involves a vacancy mechanism, with good correlation between observed and calculated activation energies (Tolchard et al. 2003). The predicted interstitial conduction pathway is a complex sinusoidal process, as shown in figure 7. An important feature is that the conduction process is aided by cooperative displacements of the silicate substructure, suggesting that the flexibility of the silicate substructure is essential to the observed high oxide ion conductivities.

In the oxygen-excess system, $\text{La}_{9.67}(\text{SiO}_4)_6\text{O}_{2.5}$ migration can be viewed as a ‘hand-over’ mechanism, whereby the interstitial oxide ion is passed from one silicate unit to another (Jones et al. 2008). More recently, MD simulations (Kendrick et al. 2008) of the germanate $\text{La}_{9.33}(\text{GeO}_4)_6\text{O}_2$ indicate that the role of

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the channel oxygen atoms appears to be as a ‘reservoir’ for the creation of mobile interstitial oxide ions, and that their migration occurs via the GeO\textsubscript{4} tetrahedra, which allows for conduction both parallel and perpendicular to the \textit{c}-axis channel.

In general, the interstitial conduction mechanism in apatites is in contrast to both fluorite- and perovskite-type SOFC materials in which oxide ion conduction proceeds through vacancy mechanisms. More recently, there is growing interest in novel ionic conductors with related structure types containing tetrahedral moieties based on doped LaNbO\textsubscript{4} (Haugsrud \& Norby 2006), LaBaGaO\textsubscript{4} (Kendrick \textit{et al.} 2007\textit{b}; Islam \& Slater 2009) and LaSrGa\textsubscript{3}O\textsubscript{7} (Kuang \textit{et al.} 2008).

5. Summary and outlook

Whatever the direction of future research, it is clear that major advances in clean energy storage and conversion technologies depend on exploring new materials, and on a greater understanding of the fundamental science of functional materials. The present survey has aimed to demonstrate the valuable role that advanced computational techniques now play in fundamental studies of energy-related materials for rechargeable lithium batteries and SOFCs.

In this context, future research on energy-related materials is likely to encompass new challenges in nano-structured materials (‘nano-ionics’) for lithium batteries, in novel ion-conducting structures/interfaces for fuel cells and in the increasing use of modelling tools to probe nano-scale and complex systems assisted by the continuing growth in hardware power.

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Batteries included


