Advanced characterization of lithium battery materials with positrons

Bernardo Barbiellini¹ and Jan Kuriplach²

¹Department of Physics, Northeastern University, Boston MA 02115, USA
²Department of Low Temperature Physics, Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, CZ-180 00 Prague, Czech Republic
E-mail: ¹b.amidei@neu.edu, ²jan.kuriplach@mff.cuni.cz

Abstract. Cathode materials are crucial to improved battery performance, in part because there are not yet materials that can maintain high power and stable cycling with a capacity comparable to that of anode materials. Our parameter-free, gradient-corrected model for electron-positron correlations predicts that spectroscopies based on positron annihilation can be deployed to study the effect of lithium intercalation in the oxide matrix of the cathode. The positron characteristics in oxides can be reliably computed using methods based on first-principles. Thus, we can enable a fundamental characterization of lithium battery materials involving positron annihilation spectroscopy and first-principles calculations. The detailed information one can extract from positron experiments could be useful for understanding and optimizing both battery materials and bi-functional catalysts for oxygen reduction and evolution.

1. Introduction
Lithium-ion batteries have played a major role in the development of portable electronics involving mobile phones, tablets and laptops because of their high energy density [1]. Clearly, design and optimization of materials are important to enable further improvements and new applications of next-generation rechargeable batteries [2]. These advances depend on studying novel compounds and gaining fundamental understanding needed to guide applied research. High throughput first-principles calculations can play a major role in characterizing and predicting the structures and properties of complex materials at the atomic scale [3]. An important goal of this effort is to establish a robust feedback loops between first-principles computations and advanced characterization based on modern spectroscopy for a rational and speedy development of lithium-ion batteries. For example, soft and hard x-ray studies performed at state-of-the-art synchrotron facilities have recently revealed useful details of lithium-ion battery function [4, 5, 6, 7, 8]. Here we show that positrons can provide unique insights in cathode materials for Li-ion batteries as well.

Positrons spectroscopy in materials science has been thoroughly described in Positron Spectroscopy of Solids [9], reviewed by Puska and Nieminen [10] and more recently by Tuomisto and Makkonen [11]. New studies involving positron spectroscopy in materials science include different systems such as topological insulators [12], PbSe quantum dots [13], tungsten surfaces coated with sodium [14], metal organic frameworks [15, 16] and also cathode materials for lithium-ion batteries [17, 18].
Layered lithium transition-metal oxide LiCoO$_2$ (LCO) and olivine-type LiFePO$_4$ (LFP) are important cathode materials. In LiFePO$_4$, the FeO$_6$ octahedron determines important features of the electronic structure related to Fe 3d electrons [4]. The CoO$_6$ octahedron plays an important role as well in the LiCoO$_2$ electronic structure. However, the O 2p character provides the dominating role for the Li$_x$CoO$_2$/Co$_2$O$_3$ in the redox orbitals [5] while the Fe 3d character dominates in the redox orbital of the LiFePO$_4$/FePO$_4$ reaction [4, 6]. When the lithium atoms are removed from the oxide matrix, Li$_x$CoO$_2$ displays complex physics involving metal/insulator transition and Li-vacancy ordering [17]. In the case of LiFePO$_4$/FePO$_4$, nanoscale phase separation is always observed. The most desired properties of cathode materials involve high redox potential, high lithium capacity and high electron and Li-ion conductivity.

2. Theory and computational method

2.1. Electron-positron correlations

The density functional theory (DFT) reduces the quantum-mechanical many-body problem to a set of manageable self-consistent one-body Schrödinger-like equations. DFT solves the electronic structure of a system in its ground state so that the electron density is the basic quantity. The DFT is generalized to positron-electron systems by including the positron density as well in the scheme as two-component DFT (TCDFT) [10]. When a positron impurity is immersed in an electron gas with density $\rho(\mathbf{r})$, the Coulomb attraction produces a screening cloud around the positron. The corresponding potential seen by the positron is constructed as

$$V_{\text{pos}}(\mathbf{r}) = V_{\text{test}}(\mathbf{r}) + V_{\text{c}}(\mathbf{r}),$$

where $V_{\text{test}}$ is the potential for a positron as a test charge and where $V_{\text{c}}$ is the polarization or correlation potential describing the positron perturbation. The correlation potential can be obtained via the Hellmann-Feynman theorem as

$$V_{\text{c}}(\mathbf{r}) = -\int_0^1 dZ \int d^3R \frac{\rho(\mathbf{R})[g(\mathbf{r}, \mathbf{R}, Z) - 1]}{|\mathbf{r} - \mathbf{R}|},$$

where $\rho(\mathbf{R})[g(\mathbf{r}, \mathbf{R}, Z) - 1]$ is the screening cloud density around a positive particle with charge Z. The local density approximation (LDA) based on accurate quantum Monte Carlo computations [19] describes the screening cloud around a delocalized positron impurity in an electron gas given by a density that varies slowly over space. The effect of the density gradient on the correlation energy can be deduced from the distortion of the polarization cloud due to this gradient. In the high density limit, the lowest order gradient correction similar to Eq. (4) of Ref. [20] reads

$$\Delta V_{\text{c}} = \frac{1}{4} \frac{e^2}{a^*} \times \beta \times f \times e.$$  (3)

In Eq. (3), the constant $\beta = 0.066725$ is calculated with the use of diagrammatic techniques in many body perturbation theory [21], the quantity $\epsilon = |\nabla \ln \rho|^2/(q_{TF})^2$ is the square of the reduced gradient (which depends on the ratio of the inhomogeneity length $1/|\nabla \ln \rho|$ and the Thomas-Fermi length $1/q_{TF}$), $e$ is the electron charge and $a^*$ is the effective Bohr radius for the electron-positron liquid. The distance $a^*$ is given by the Bohr radius $a_B$ renormalized by an effective mass $a^* = a_B/\mu$. For a liquid where the positron density equals the electron one [22] the effective mass is given by $\mu = 1/2$ and this relationship remains approximately correct also in the limit of the positron impurity [23, 24, 25]. The factor $f$ depends on the fraction of positrons in the electron-positron liquid and is similar for the rescaling for spin polarization used in Ref. [20]. When the positron is an impurity, $f = 1/2$. Whereas equality of the positron and electron densities implies $f = 1$. Therefore, the difference between the electronic gradient

1 In fact we employ $\epsilon = 4t^2$, $t$ being the reduced gradient as it is usually defined (see Ref. [20]).
correction of Eq. (4) in Ref. [20] and Eq. (3) is given by the factor \( f \times \mu = 1/4 \). In order to interpolate to the case of rapid density variations (i.e. large \( \epsilon \)), we use the formula of the parameter-free generalized gradient approximation (GGA) [26]

\[
V_c(r) = V_c^{LDA}(r) \exp\left[-\alpha(r) \epsilon(r)/3\right],
\]

where \( \alpha \) is a function of the local density given by

\[
\alpha(r) = -\frac{3}{16} \frac{\beta}{V_c^{LDA}(r) a_B} \epsilon^2.
\]

The corresponding electron-positron enhancement factor is

\[
\gamma - 1 = (\gamma_{LDA} - 1) \exp(-\alpha\epsilon).
\]

2.2. Calculations of electronic structure and positron properties

The electronic structure of the studied Li\(_x\)CoO\(_2\), NaCoO\(_2\) and Li\(_x\)FePO\(_4\) materials was determined using the WIEN2k code [27]. This code is an implementation of the augmented plane-wave plus local orbital (APW+lo) method, which is considered to be one of the most accurate techniques to calculate electronic structure of solids. In these calculations, a GGA exchange-correlation functional for electrons after Perdew, Burke, and Ernzerhof [20] was employed. In the case of Li\(_x\)FePO\(_4\) system, we investigated the influence of the Hubbard \( U \) parameter on the electronic structure and took its values values from Ref. [28] performing thereby GGA+\( U \) calculations. The selfconsistent electron density and Coulomb potential were taken from electronic structure calculations in order to construct the positron potential (including its correlation part discussed above). The Schrödinger equation for positron is then solved on a 3D regular mesh covering the unit cell of studied materials. Full computational details are given in Ref. [29].

LiCoO\(_2\) has a layered structure of O3-type. The structural parameters for the corresponding rhombohedral unit cell were taken from Ref. [30]. NaCoO\(_2\), which we have examined too as a possible cathode material, is isostructural with LiCoO\(_2\), and we used structural parameters from Ref. [31]. The structure of Li\(_x\)CoO\(_2\) and NaCoO\(_2\) is shown in figure 1 where alternating Li (or Na), O and Co layers are well seen. The Co, O and alkali ions (Li or Na) are represented by blue, red and yellow spheres, respectively. For the sake of simplicity, we employed the same structure for partially delithiated system Li\(_{0.5}\)CoO\(_2\), removing just some Li atoms to represent vacancies. No structure relaxation was performed.

Following our study on oxides based on the parameter-free GGA [32], we have calculated the sum \( A^+ \) of the electron and positron chemical potentials (called usually positron affinity) and the positron lifetime, \( \tau \), in Li\(_x\)CoO\(_2\), NaCoO\(_2\) and Li\(_x\)FePO\(_4\) within the TCDFT framework. In particular, \( \tau \) was calculated via the positron annihilation rate \( (1/\tau) \) according to the formula

\[
\frac{1}{\tau} = \pi r_0^2 c \int d\mathbf{r} \rho^+(\mathbf{r}) \rho(\mathbf{r}) \gamma[\rho(\mathbf{r}), \epsilon(\mathbf{r})],
\]

where \( r_0 \) and \( c \) are the classical electron radius and speed of light, respectively. The spatial integration proceeds over the unit cell. The positron density is obtained simply as \( \rho^+ = |\psi^+|^2 \) from the properly normalized positron ground state wave function \( \psi^+ \).

3. Results

In our previous study on oxides [32], we have shown the crystal structures of LiFePO\(_4\) and FePO\(_4\) together with the corresponding isosurface occupied by the positron density distribution (PDD) \( \rho^+(\mathbf{r}) = |\psi^+(\mathbf{r})|^2 \). We have observed that in FePO\(_4\) the positron density occupies one-dimensional channels where Li is located in LiFePO\(_4\). Therefore, positrons studies should
facilitate the understanding of the Li atom transport. We provide here a similar visualization on the positron density in the CoO$_2$ matrix with Li and Na intercalation. In figures 2-3, the Co, O and alkali ions (Li or Na) are represented in the same way as in figure 1, whereas the isosurfaces of the positron density are colored in dark yellow (all figures). The ‘vertical’ red surfaces reflect the variation of $\rho^+$ along a vertical plane at the corresponding simulation box side.

The PDD in LiCoO$_2$ shown in figure 1 (left part) is more concentrated in the Li planes compared to the PDD of NaCoO$_2$ displayed also in figure 1 (right part). In NaCoO$_2$ the positron samples more the adjacent O planes. In the case of LiCoO$_2$, $\tau = 131.0$ ps and $A^+ = -5.30$ eV while $\tau = 119.7$ ps and $A^+ = -6.61$ eV for NaCoO$_2$. Therefore the substitution of Li by Na gives significant differences both for the lifetime (a decrease by $\sim 10$ ps) and $A^+$ (a decrease by $\sim 1.3$ eV). It is surprising to see that positrons have less affinity for LiCoO$_2$ and at the same time live longer in this material, which is due to positron redistribution compared to NaCoO$_2$.

The positron wave function is significantly modified by delithiation. This effect corresponding to $x = 0.5$ is demonstrated in figure 2 for two cases. When the Li vacancies do not cluster and are evenly distributed in each Li plane, positrons occupy equally each such plane (see the left part of figure 2). In this case, $\tau = 179.2$ ps and $A^+ = -8.23$ eV. Oppositely, $\rho^+$ is distributed mainly in the Li vacancy cluster and not in planes with no or smaller amount of Li vacancies, as it is illustrated in the right part of figure 2. Consequently, the lifetime increases to 214.0 ps and $A^+$ decreases to $-9.99$ eV.

It is also instructive to inspect what happens if Li is completely removed from the lattice. The Li$_x$CoO$_2$ (and Na$_x$CoO$_2$) systems become pure CoO$_2$. In such a case, the lattice dimension perpendicular to Li (or Na) layers somewhat shrinks and the amount of open space in the structure decreases. Nevertheless, the
positron lifetime remains quite long (151.0 ps) and $A_+$ value $-8.98$ eV is about in the middle between $x = 0.5$ cases just discussed. This is caused by quite large ‘empty’ planes between CoO$_2$ layers, which can be deduced from figure 3 where positron density distribution is plotted. Complete delithiation does not occur in commercial LCO batteries, but it is possible to achieve it in a laboratory experiment [33] (from where we also took lattice parameters for CoO$_2$).

Finally, table 1 gives lifetimes $\tau$ and chemical potentials sums $A^+$ for various magnetic configurations of LiFePO$_4$ and FePO$_4$. The positron lifetime changes dramatically with lithiation but remains rather insensitive to the magnetic structure. However, as illustrated by table 1, measurements of $A^+$ could be very useful to benchmark theoretical models involving various magnetic configurations and the Hubbard parameter $U$. Moreover, the variation $\Delta A^+ = A^+(x=0) - A^+(x=1)$ upon delithiation ($3.5$ eV for the AFM case) appeared to be related to the redox potential [28]. Since the positron chemical potential does change significantly with Li intercalation, $\Delta A^+$ yields mostly the variation of the electron chemical potential.

| $x$ | Magnetic structure | Lifetime $\tau$ (ps) | $A^+$ (eV) |
|-----|--------------------|----------------------|------------|
| 1   | NM                 | 169.4                | -6.32      |
| 1   | FM                 | 169.1                | -5.75      |
| 1   | AFM                | 169.7                | -5.70      |
| 1   | FM+U               | 169.1                | -6.87      |
| 0   | NM                 | 205.0                | -9.00      |
| 0   | FM                 | 205.8                | -9.13      |
| 0   | AFM                | 207.2                | -9.37      |
| 0   | FM+U               | 206.4                | -9.91      |

4. Conclusion
The parameter-free GGA method predicts that spectroscopies based on positron can be deployed to detect the elusive lithium in the oxide matrix of Li-batteries. The positron lifetime $\tau$ changes dramatically with lithiation and provide information about the space available for Li migration. Nevertheless, the interpretation of existing lifetime data [17, 18] for both Li$_x$CoO$_2$ and Li$_x$FePO$_4$ is challenging due to the complicated microstructure of the studied samples. Measurements of $A^+$ could be very useful to benchmark various theoretical models and the variation of $A^+$ upon delithiation could be used to determine redox potentials. Similar advanced characterization can be deployed in related materials used as bifunctional catalysts for oxygen reduction and oxygen evolution reactions [34].

Acknowledgments
The work at Northeastern University was supported by the US Department of Energy (DOE), Office of Science, Basic Energy Sciences grant number DE-FG02-07ER46352 (core research), and benefited from Northeastern University’s Advanced Scientific Computation Center (ASCC), the NERSC supercomputing center through DOE grant number DE-AC02-05CH11231, and support (applications to layered materials) from the DOE EFRC: Center for the Computational Design of Functional Layered Materials (CCDM) under DE-SC0002575. J. K. acknowledges the support by the Ministry of Education, Youth and Sports of the Czech Republic from
the Large Infrastructures for Research, Experimental Development and Innovations project “IT4Innovations National Supercomputing Center – LM2015070”.

References

[1] Goodenough J B and Kim Y 2010 Chem. Mater. 22 587
[2] Islam M S and Fisher C A J 2014 Chem. Soc. Rev. 43 185
[3] Ceder G and Persson K 2013 How supercomputers will yield a golden age of materials science Scientific American 309(6) 34
[4] Liu X, Liu J, Qiao R, Yu Y, Li H, Suo L, Hu Y-S, Chuang Y-D, Shu G, Chou F, Weng T-C, Nordlund D, Sokaras D, Wang Y J, Lin H, Barbiellini B, Bansil A, Song X, Liu Z, Yan S, Liu G, Qiao S, Richardson T J, Prendergast D, Hussain Z, de Groot F M F and Yang W 2012 J. Am. Chem. Soc. 134 13708
[5] Mizokawa T, Wakisaka Y, Sudayama T, Iwai C, Miyoshi K, Takeuchi J, Wada H, Hawthorn D G, Regier T Z and Sawatzky G A 2013 Phys. Rev. Lett. 111 056404
[6] Liu X, Wang Y J, Barbiellini B, Hafiz H, Basak S, Liu J, Richardson T, Shu G, Chou F, Weng T-C, Nordlund D, Sokaras D, Moritz B, Devereaux T P, Qiao R, Chuang Y-D, Bansil A, Hussain Z and Yang W 2015 Phys. Chem. Chem. Phys. 17 26369
[7] Suzuki K, Barbiellini B, Orikasa Y, Go N, Sakurai H, Kaprzyk S, Itoh M, Yamamoto K, Uchimoto Y, Wang Y J, Hafiz H, Bansil A and Sakurai Y 2015 Phys. Rev. Lett. 114 087401
[8] Suzuki K, Barbiellini B, Orikasa Y, Kaprzyk S, Itoh M, Yamamoto K, Wang Y J, Hafiz H, Uchimoto Y, Bansil A, Sakurai Y and Sakurai H 2016 J. Appl. Phys. 119 025103
[9] 1995 Positron Spectroscopy of Solids ed A Dupasquier and A P Mills Jr (Amsterdam: IOS Press)
[10] Puska M J and Nieminen R M 1994 Rev. Mod. Phys. 66 841
[11] Tuomisto F and Makkonen I 2013 Rev. Mod. Phys. 85 1583
[12] Callewaert V, Shastry K, Sanitè R, Makkonen I, Barbiellini B, Assaf B A, Heiman D, Moodera J S, Partoens B, Bansil A and Weiss A 2016 Phys. Rev. B 94 115411
[13] Shi W, Ejit S W H, Sandeep Suchand C S, Siebbeles L D A, Houtepean A J, Kinge S, Brück E, Barbiellini B and Bansil A 2016 Phys. Rev. B 93 081602
[14] Terabe H, Iida S, Yamashita T, Tachibana T, Barbiellini B, Wada K, Machiuzuki I, Yagishita A, Hyodo T and Nagashima Y 2015 Surf. Sci. 641 68
[15] Crivelli P, Cooke D, Barbiellini B, Brown B L, Feldbyum J I, Guo P, Gidley D W, Gerchow L and Matzger A J 2014 Phys. Rev. B 89 241103(R)
[16] Jones A C L, Goldman H J, Zhai Q, Fang P, Tom H W K and Mills A P Jr 2015 Phys. Rev. Lett. 114 153201
[17] Parz P, Fuchsbichler B, Koller S, Bitschmab B, Mautner F A, Puff W and Würschum R 2013 Appl. Phys. Lett. 102 151901
[18] Zhang P, Wang Y, Lin M, Zhang D, Ren X and Yuan Q 2012 J. Electrochem. Soc. 159 A402
[19] Drummond N D, López Ritos P, Needs R J and Pickard C J 2011 Phys. Rev. Lett. 107 207402
[20] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[21] Ma S-k and Brueckner K A 1968 Phys. Rev. 165 18
[22] Brinkman W F, and Rice T M 1973 Phys. Rev. B 7 1508
[23] Leung C H, Stott M J and Almbladh C O 1976 Phys. Lett. A 57 26
[24] Jarlborg T and Singh A K 1987 Phys. Rev. B 36 4660
[25] Drummond N D, López Ritos P, Pickard C J and Needs R J 2010 Phys. Rev. B 82 035107
[26] Barbiellini B and Kuriplach J 2015 Phys. Rev. Lett. 114 147401
[27] Blaha P, Schwarz K, Madsen K G K, Kvasnicka D and Luitz J 2001 WIEN2k: An Augmented Plane Wave and Local Orbitals Program for Calculating Crystal Properties (Vienna University of Technology, Vienna, Austria).
[28] Zhou F, Cococcioni M, Marianetti C A, Morgan D and Ceder G 2004 Phys. Rev. B 70 235121
[29] Kuriplach J and Barbiellini B 2014 Phys. Rev. B 89 155111
[30] Takahashi Y, Kijima N, Dokko K, Nishizawa M, Uchida I and Akimoto J 2007 J. Sol. State Chem. 180 313
[31] Vicu L, Bos J W G, Zandbergen H W, Huang Q, Foo M L, Ishiwata S, Ramirez A P, Lee M, Ong N P and Cava R J 2006 Phys. Rev. B 73 174104
[32] Kuriplach J and Barbiellini B 2016 Parameter-free gradient correction for positron states in oxides Mater. Sci. Forum (accepted, Proceedings of ICPA-17)
[33] Venkatraman S and Manthiram A 2002 Chem. Mater. 14 3907
[34] Maiyalagan T, Jarvis K A, Therese S, Ferreira P J and Manthiram A 2014 Nat. Commun. 5 3949