The voltage is a key parameter for the performance of Li-ion cells. An increased average voltage results in a higher energy- and power density. Theoretically, the potential of Li-intercalation electrodes is related to the chemical potentials of both electrons and Li\(^+\) ions, and the voltage of a cell to their respective differences. As experimentally these quantities cannot be directly obtained, the exact contribution of electrons and Li\(^+\) ions to the voltage is still not known for the different materials. In this contribution, we investigate the correlation of the average cell voltage with the electronic ionization potential of different thin film cathode materials. Specifically, we relate the ionization potential obtained by photoelectron spectroscopy to the electron chemical potential at the onset of the charging plateau, and its difference to the ionization potential of lithium to the electronic contribution of the cell voltage. As experimental data both layered and olivine cathode materials are considered and we find a reasonable correlation between ionization potential and average voltage, as well as the electronic contribution as major factor for the battery voltage. The possible reasons for the deviation such as the ionic contribution and the presence of surface dipole potentials are discussed.

The performance of Li-ion batteries can be improved by a higher specific capacity and/or a higher average cell voltage.\(^1\) The voltage of a Li-ion cell is determined by the free enthalpy of the lithium exchange reaction, which consists of Li-intercalation and deintercalation reactions at the active electrode materials. Several approaches can be adopted for the consideration of these reactions and the related electrode potentials, which include to different extents the involvement of electrons, ions as well as interaction (solid state) effects (see e.g. Refs. 3–5,6). On a first sight, the partial reactions may be perceived just as simple redox reactions, where for a common cathode material the transition metal (TM) ions act as a redox couple. However, such a view does not consider solid state effects and the interaction of electrons and ions in the solid matrix.\(^5\) Important consequences of these effects are that the electronic states of the TM ions involved in the reaction are dependent on the degree of intercalation and that simple Nernst behavior is commonly not observed.

For this reason, we have considered an alternative approach to discuss the value of the electrode potential looking at the electron and ion transfer into the solid state material of the electrodes. The Fermi level and the electronic structure of the electrodes is given by the electronic density of states (DOS),\(^3\)\(^6\) Fig. 1. Under normal operation conditions, the Fermi level of a common cathode material is usually located in a TM-3d derived band and shifts upon change of state of charge as the band is filled or depleted upon intercalation or deintercalation, respectively. The shifts in Fermi level can thereby be related to corresponding shifts in the electron chemical potential.\(^8\) However, this approach does not consider the specific bonding of the Li-ions in the electrode, i.e. it does not capture any differences of Li-ion chemical potential with respect to lithium metal or any other anode material.

Most accurate, the voltage of a Li-ion cell is expressed by the change of the Gibbs free energy \(\Delta G\), or the difference in Li chemical potential between cathode and anode (\(\mu_{Li}^+\), \(\mu_{Li}^-\)), respectively:\(^6\)\(^7\)\(^8\)

\[
U_{scv} = \frac{-\Delta G}{zF} = \frac{\mu_{Li}^+ - \mu_{Li}^-}{zF} = \frac{\Delta \mu_e + \Delta \mu_{Li}^-}{zF},
\]

where \(z\) is the charge transferred between the electrodes (here 1) and \(F\) is the Faraday constant.

Formally, one may separate the chemical potential of the lithium, which is exchanged between the two electrodes, into the (electro) chemical potentials of the electrons \(\Delta \mu_e\), and the ions \(\Delta \mu_{Li}^-\), which provides the extended version of Eq. 1, describing the change of the Gibbs energy of cathode and anode and their difference in dependence of electron and ion exchange. The electronic contribution is generally assumed to play a dominating role.\(^6\)\(^8\) This is indicated for example via the substitution of transition metals in olivine materials resulting in a higher average voltage if the TM ion with a higher ionization potential are used\(^10\) or by our experiments on replacing O\(^2\)- anion with P\(_2\)O\(_5\)- poyanion.\(^11\) Also our measurements on thin film intercalation electrodes using in-situ or operando set-ups support this conclusion.\(^12\)\(^15\)\(^16\) To gain insight into the fundamental processes of electron and ion exchange in solid electrodes and related changes in battery performance for battery materials, first principle calculations were developed over the last two decades (see e.g. Refs. 8,17,18) fol-
allowing the systematic work of Ceder et al.\textsuperscript{19,20} However, systematic experimental studies on the relative influence of the electronic and ionic contributions on the measurable battery voltage have not been performed mostly due to experimental difficulties.

Principally, the electrochemical potential of the electrons as defined by the energy difference of the vacuum level to the Fermi level inside the solid (Refs. 6,21) can be determined via measurement of the electronic work function by a number of experimental techniques such as photoelectron spectroscopy. However, the electron chemical potential as meaningful quantity cannot be rigorously extracted from such data due to the unknown value of the surface double layer potential.\textsuperscript{6,23} Nevertheless, the electron and Li-ion chemical potential, which could be extracted from a Li-ion work function measurement and a known value of the surface potential.\textsuperscript{6,23} The NaCoO\textsubscript{2} thin film cathode materials were prepared on a NASICON substrate by using pulsed laser deposition (PLD).\textsuperscript{16} The LiFePO\textsubscript{4} composite cathode was synthesized by using the Pechini method.\textsuperscript{26} The sample preparation is necessary for the sample’s crystallization of layered- and olivine- structures to reach the R-3m and Pnma space group symmetry, respectively. The details of the sample’s preparation are reported elsewhere.\textsuperscript{11,16,25–30}

Photoemission experiments on the study of the electronic properties of the thin film layered- and olivine structure cathodes were performed at the Darmstadt Integrated System for Battery Research (DAISY-BAT) equipped with an XPS/UPS spectrometer (Phi 5000 Versa Probe). A conventional monochromatic Al K\textsubscript{α} (hv = 1486.6 eV) source, as well as He I (hv = 21.2 eV) and He II (40.8 eV) sources were used at DAISY-BAT for in-situ interface experiments. The secondary electron cutoff (SEC) was measured by using hv = 21.2 eV and applying a negative bias voltage of 6 V. The electronic structure of the LiFePO\textsubscript{4}-composite was measured by using synchrotron facilities of BESSY II (Berlin) at the U49-2/PGM-2 undulator beamline with a plane grating monochromator with an accessible energy range of hv = 100–1900 eV. The beamline was equipped with Solid Liquid Interface Analysis (SoliAS) endstation and a SPECS PHOIBOS 150 MCD-9 electron analyzer.\textsuperscript{31} Photon energies were varied to yield photoelectrons from the same analyzed depth. The binding energies were referred to the Fermi level of an Ag- or an Au- polycrystalline foil.

Results and Discussion

The schematic energy diagram of a complete battery cell deduced by using our surface science approach is shown in Fig. 2. The valence band and core level spectra of cathodes, anodes and solid electrolytes, as well as their values of work function before and after being brought into contact are obtained from the photoemission interface experiments. In such experiments the alignment of energy levels across the cathode/electrolyte and anode/electrolyte interface is measured. By comparing the relative shift of the valence band maximum, $E_V$, and the work function, $W_f$, as well as by analyzing the band bending

![Figure 2. Schematic electronic energy level diagram of a Li-ion battery cell, as deduced from photoemission interface experiments of a LCO/LiPON/Li cell.\textsuperscript{36}](Image)

The LCO thin film intercalation cathode is in a discharged state. $E_V$, $E_{Vac}$, IP, $E_F$, $W_{f,c}$, $W_{f,Li}$, $E_F$ and emf are the valence band maximum, vacuum level, ionization potential, conductive band, work function of the cathode, work function of lithium metal, Fermi level and electromotoric force, respectively. $\epsilon_{f,Li}$ and $\epsilon_{f,c}$ are the surface dipole formed on lithium metal and cathode, respectively. The differences in the vacuum levels, $\Delta E_{Vac}$, at the interfaces occur due to the differences in Li-ion chemical potentials and electric potential drops. On the right side, the valence band region of a pristine LCO thin film is shown.
The valence band spectra of the transition metal oxides layered- (a) and olivine type- (b) structure cathodes as prepared, i.e. not electrochemically delithiated. The valence band maximum, $E_V$, is determined by linear extrapolation of the valence band edge to the baseline, giving the onset energy of bound electrons, $E_V-E_F$. This onset energy, shown by the dash line (b), evidences the trend in the increasing of the ionization potential of the cathode materials via substitution of Fe$^{2+}$ by Co$^{3+}$ and Ni$^{2+}$, therefore, the resulting in increase of average voltage, $V_{oc}$, of the battery cells.

The aim of this paper is to investigate the correlation between the electrode potential and the electron chemical potential using the results obtained on several cathodes of different crystal structure and different redox potentials, such as the ATMO$_2$ ($A$ = Li, Na; TM = Co, Ni) layered- and LiTMPO$_4$ (TM = Fe, Co, Ni) olivine- materials. For this purpose the energetic position of the valence band onset of the cathode material vs. vacuum level must be known (see Fig. 3). As mentioned previously, the electron chemical potential is related to the work function and Fermi level position, respectively. For fully discharged (fully lithiated) cathode thin film materials, the Fermi level position is somewhere midgap indicating that the material can be treated as semiconductors. Therefore, the Fermi level will generally be dependent on the presence of defects associated with doping of materials or the preparation conditions. This emphasizes the importance of clean and well-defined cathode materials (see also Refs. 11–16,22,24,25,27–30,36). In any case, the dependence of the Fermi level on the preparation conditions must be taken account for the comparison of different materials introducing additional uncertainties in the correlation between electrode potential and electron chemical potential if not experimentally determined. The ionization potential is directly related to the valence band structure of the host material and it is not affected by minor changes of defect concentrations in contrast to the Fermi level.\(^{27}\) Its energetic position can be deduced from the valence band spectra; it holds $I_p \equiv W_I + (E_V-E_F)$. Within the conceptual framework of chemical potentials, the ionization potential is related to the (electro)chemical standard potential of the electrons as can be concluded e.g. from Ref. 5.

Figure 4 shows the dependence of the open circuit voltage on the charge state for a battery cell, illustrating the relationship between the plateau values of the electrode potentials and the ionization potentials via plotting the energy diagrams of the cathode at a certain charged state. In the discharged state, which corresponds to the area 1 of the voltage curve (Fig. 4), the Fermi level is situated between the highest occupied state and the lowest unoccupied state, i.e. in the bandgap (Fig. 4), which is the fundamental property of semiconductors. Withdrawal of a Li$^+$ ion from the cathode upon charging is coupled to release of a valence electron to maintain charge neutrality of the system. The resulting hole is situated at the TM-3d state, which leads to the Fermi level shift toward the occupied states. It is reasonable to assume that the onset of the charge plateau can be identified with the situation that the Fermi level reaches and starts to cross the valence band edge. At this charging state, Fermi level and ionization potential become equal (Fig. 4, the area 2). Table I summarizes the values of the valence band onset ($E_V-E_F$), the ionization potential ($I_{p,cathode}$) and work function ($W_I$) obtained from our experimental studies from the...
The ionization potential of lithium metal was reported, which could be motivated by the fact that the work function tends to be strongly influenced by surface dipole contributions. For metals, a surface dipole increasing the work function is theoretically expected, and for lithium metal calculations indicate a fairly high value. Uncertainties in defining the lithium work function occur due to the temperature dependence of Wf as well as the presence of common impurities in lithium such as Na and K etc. This is probably the main reason of a large scatter in the reported values of the work function determined by different experimental techniques, which lay in the wide range (1.4 – 2.93 eV). For oxides, the orientation and values of surface dipoles are highly dependent on surface constitution and preparation conditions, so that their contribution cannot be reliably assessed. In our recent research, we have discussed the presence of the intrinsic surface defects and their crucial role on the electronic properties of the layered structure oxides. Concerning the ionic contributions, our previous work demonstrates that they generally play a role (see also discussion further below). And we tentatively assign the differences in the deviation between different material classes mostly to this effect. In this regard, it is worth noting the Li\textsubscript{2}V\textsubscript{2}O\textsubscript{5} orthorhombic structure cathode, where the estimated ionization potentials difference is slightly higher compared to the nominal voltage of 3.3 V for Li\textsubscript{2}V\textsubscript{2}O\textsubscript{5} primary battery (see below). However, we also cannot neglect inaccuracies in the experimental data and possible inconsistencies in our approach comparing solid/vacuum interfaces to solid/electrolyte interfaces, where different dipolar potential layers must be expected. For electrochemical interfaces, specific adsorption and double layer formation induce dipolar effects and electrostatic potential drops, respectively, resulting in a shift of energy levels at the interface. Again, an educated guess is hardly possible e.g. comparing the oligine compounds and layered oxides without further systematic studies. For adsorption of organic solvents on layered oxide cathodes, for example, we observed electrostatic potential drops as high as 0.8 eV. Despite these uncertainties, our approach provides a rather reasonable estimate of the battery voltages and can be taken as additional argument that the electronic charge transfer provides the larger part of the battery voltage at least for alkali intercalation electrodes. These conclusions are supported also by our results obtained on layered chalcogenides, and the Li\textsuperscript{+} intercalation of V\textsubscript{2}O\textsubscript{5} film. A value of ΔE\textsubscript{cathode-Li} = 3.8 ± 0.3 eV was estimated for Li\textsubscript{2}V\textsubscript{2}O\textsubscript{5} (x = 2.4 ± 0.4) film, taking into account W\textsubscript{Li\textsuperscript{2}V\textsubscript{2}O\textsubscript{5}} = 5.6 eV, E\textsubscript{V(3d)} - E\textsubscript{F} = 0.7 eV±0.1 eV, and IP\textsubscript{Li} = 2.49 eV. Here, the W\textsubscript{Li\textsuperscript{2}V\textsubscript{2}O\textsubscript{5}} does not include an additional surface dipole (~1.4 eV) induced by a partial Li\textsuperscript{+} adsorption, which was subtracted from the work function. The most accurate results on the driving force of intercalation and their correlation with battery voltage are expected from operando experiments with a solid state battery arrangement, since such experiments minimize an external impact associated with possible surface contaminations, which is hard to avoid for quasi in-situ or even ex-situ experiments. Operando photomission experiments to study the changes of
The electronic structure vs. the battery voltage were already carried out on TiS$_2$ and later on Na$_2$CO$_3$. By the study of the layered chalcogenide, it was suggested that about 60% of the thermodynamic driving force of intercalation can be related to the electron exchange.

Recently, the absolute values of the electronic work function and ionic work of LiCoO$_2$ were determined by using independent techniques without reference to a counter electrode (see Ref. 9). The electronic work function has been found to be a larger part of the overall bonding of Li atoms.

Conclusions

Our results obtained on pristine, surface layer free thin film electrodes demonstrate that the average battery voltage correlates reasonably well with the difference of the electronic ionization potential, showing that the electronic contribution to the electrode potential is the main factor in agreement with concepts proposed by Gerischer et al. Thus we conclude that the performance of Li-ion batteries depends on the relative changes of bonding contributions for electrons and ions within the solid structure of the used electrodes with electrons providing the larger part to the battery voltage. The experimentally observed variations in the ionization potential difference as compared to the average voltage must be related to deviations of the rigid band behavior of the electrode materials and to surface effects occurring in the given battery set-up. Here, the ionic contribution is significant and cannot be completely neglected. Thus for a more rigorous analysis, also surface dipolar potentials and for electrodes in a higher charge state the evolution of the electronic structure needs to be considered (rigid band vs. non-rigid band behavior).

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References

1. T. Placke, R. Kloepsch, S. Dühnen, and M. Winter, J. Solid State Electrochem., 21(7), 1939 (2017).
2. B. C. Melot and J. M. Tarascon, Acc. Chem. Res., 46(5), 1226 (2013).
3. J. B. Goodenough and Y. Kim, Chem. Mater., 22(3), 587 (2010).
4. T. Ohzuku and A. Ueda, J. Electrochem. Soc., 144(8), 2780 (1997).
5. W. R. McKinnon, Insertion electrodes I: Atomic and electronic structure of the hosts and their insertion compounds, in Solid State Electrochemistry, P. G. Bruce, Editor. 1995, Cambridge University Press: Cambridge.
6. H. Gerischer, F. Becker, and B. Scrosati, J. Electrochem. Soc., 141(9), 2297 (1994).
7. J. R. Owen, Chem. Soc. Rev., 26, 259 (1997).
8. A. Urban, D. H. Seo, and G. Ceder, Npj Comput. Mater., 2, 9 (2016).
9. S. Schuld, R. Hausbrand, M. Fingerle, W. Jaegermann, and K.-M. Weitzel, Adv. Energy Mater., 8, 1703411 (2018).
10. A. K. Gadhi, K. S. Nanjundaswamy, and J. B. Goodenough, J. Electrochem. Soc., 144, 1188 (1997).
11. G. Cherkashinin, S. U. Sharath, and W. Jaegermann, Adv. Energy Mater., 7, 1602321 (2017).
12. D.Entsling, G. Cherkashinin, S. Schmid, S. Bhuvaneswari, A. Thiesen, and W. Jaegermann, Chem. Mater., 26, 3948 (2014).
13. G. Cherkashinin, M. V. Lebedev, S. U. Sharath, A. Hajduk, S. Nappini, and E. Magnano, J. Mater. Chem. A, 6, 4966 (2018).
14. C. Guhl, P. Kehne, Q. Ma, F. Tietz, L. Alff, P. Komissinskiy, W. Jaegermann, and R. Hausbrand, Rev. Sci. Instrum., 89, 0737104 (2018).
15. S. P. Fong, V. L. Chevrier, G. Hautier, A. Jain, C. Moore, S. Kim, X. Ma, and G. Ceder, Energy Environ. Sci., 4(9), 3680 (2011).
16. M. Saubanere, E. McCalla, J.-M. Tarascon, and M.-L. Doublet, Energy Environ. Sci., 9(3), 984 (2016).
17. G. Ceder, M. K. Aydiln, and A. F. Kohan, Comput. Mater. Sci., 81(1–2), 161 (1997).
18. M. K. Aydiln, A. F. Kohan, G. Ceder, K. Cho, and J. Joannopoulos, Phys. Rev. B, 56(5), 1354 (1997).
19. N. Sato, Electrochemistry at Metal and Semiconductor Electrodes, 2003, Amsterdam: Elsevier Science B.V.
20. R. Hausbrand, G. Cherkashinin, M. Fingerle, and W. Jaegermann, J. Electron. Spectrosc. Relat. Phenom., 221, 65 (2017).
21. J. Maier, Solid State Ionics, 143, 17 (2001).
22. G. Cherkashinin, D. Entsling, P. Komissinskiy, R. Hausbrand, and W. Jaegermann, Surf. Sci., 608, L13 (2013).
23. G. Cherkashinin, D. Entsling, and W. Jaegermann, J. Mater. Chem. A, 2, 3571 (2014).
24. L. Demosse, S. Jacke, C. Spanheimer, and W. Jaegermann, J. Alloys Comp., 509, 3777 (2011).
25. G. Cherkashinin, D. Entsling, A. Thiesen, S. Laubsch, P. C. Schmidt, and W. Jaegermann, Phys. Rev. B, 82, 195431 (2010).
26. D. Becker, G. Cherkashinin, R. Hausbrand, and W. Jaegermann, J. Phys. Chem. C, 118, 962 (2014).
27. G. Cherkashinin and W. Jaegermann, J. Chem. Phys., 144, 184706 (2016).
28. G. Cherkashinin, R. Eilhardt, M. V. Lebedev, S. Nappini, E. Magnano, and W. Jaegermann, J. Electrochem. Soc., 165, H3143 (2018).
29. T. Meyer, V. Lebedev, R. Hunger, and W. Jaegermann, Appl. Surf. Sci., 252, 31 (2005).
30. R. Hausbrand, G. Cherkashinin, H. Ehrenberg, M. Gröting, K. Albe, C. Hess, and W. Jaegermann, Mater. Sci. Engineer. B, 192, 3 (2015).
31. R. Hausbrand, G. Cherkashinin, M. Fingerle, and W. Jaegermann, J. Electron Spectrosc. Relat. Phenom., 221, 65 (2017).
32. R. Hausbrand, D. Becker, and W. Jaegermann, Prog. Solid State Chem., 42(4), 175 (2014).
33. D. Entsling, C. Pettenkofer, and W. Jaegermann, Ionics, 6, 196 (2000).
34. A. Schöwelb, W. Jaegermann, and R. Hausbrand, Solid State Ionics, 288, 224 (2016).
35. S. Kashiwaya, T. Toupane, A. Klein, and W. Jaegermann, Adv. Energy Mater. (2018).
36. P. A. Anderson, Phys. Rev., 75, 1205 (1949).
37. N. D. Lang and W. Kohn, Phys. Rev. B, 3, 1215 (1971).
38. H. B. Michaelson, J. Appl. Phys. 48, 4729 (1977).
39. N. D. Lange and W. Kohn, Physical Rev., 81, 4555 (1970).
40. N. D. Lange and W. Kohn, Physical Rev., 83, 1215 (1971).
41. B. B. Alchagirov, L. Kh. Afaunova, F. F. Dyshekova, and R. Kh. Arkhestov, Technical Physics, 60, 292 (2015).
42. A. Klein, J. American Ceramic Society, 99(2), 369 (2016).
43. A. Klein et al., Thin Solid Films, 518, 1197 (2009).
44. D. Becker et al., J. Phys. Chem. C, 118(2), 962 (2014).
45. R. Hausbrand et al., Thin Solid Films, 643, 43 (2017).
46. Q.-H. Wu, A. Thiessen, and W. Jaegermann, Surf. Sci., 578, 203 (2005).
47. Guhl et al., in preparation.
48. H. Arai, S. Okada, Y. Sakurai, and J.-ichi Yamaki, Solid State Ionics, 109, 295 (1998).
49. S. Goto Nakayama, Y. Uchimoto, M. Wakahara, and Y. Kitajima, Chem. Mater., 16, 3399 (2004).
50. J. Wolfenstein and J. Allen, J. Power Sour., 142, 389 (2005).
51. W. Yang, Z. Wang, L. Chen, Y. Chen, L. Zhang, Y. Lin, J. Li, and Z. Huang, RSC Adv., 7, 33680 (2017).

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