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Description	

The role of intermolecular polarization for the stability of lithium intercalation compounds of α - and β -perylene

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Lithium intercalation compounds of α - and β -perylene are investigated by photoelectron spectroscopy. Spectroscopic data together with a Born-Haber cycle provide information on the formation enthalpy of those materials. This approach allows understanding the amount of charge transferred from the alkali metal atoms to the π system, and illuminates the role of molecular versus solid-state properties in the formation of the intercalation compounds. In the bulk of α -perylene material, molecular dimerization survives upon intercalation which reduces the Madelung energy of the intercalation compound but increases the electron-accepting capability of the organic system and facilitates the ionization of lithium atoms in the molecular solid environment. The lower ionization potential results in a larger charge transfer (about two electrons per molecule) in α -perylene compared to the monomeric system, β -perylene. © 2004 American Institute of Physics.

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I. INTRODUCTION

Lithium-ion batteries based on carbon π -electronic systems provide high volumetric and gravimetric energy densities, high capacities, and rechargeability.¹⁻³ The reason for using lithium cations is their high charge/radius ratio compared to the other alkali metals which provides fast ionic conduction into solid electrodes and through the electrolyte separating the two electrodes. In such batteries, upon charging, Li^+ ions are transported from the positive electrode via the electrolyte to the carbon-based (or organic) electrode where they are intercalated to form charge-transfer compounds. Since the charge state of the lithium atoms is not changed in this process, it is the relative stability of the two Li-intercalated electrode materials which determines the maximal possible amount of energy to be stored and the electrochemical potential difference between the two electrode materials.

Electrochemical intercalation is not the only way to intercalate lithium into an organic material. The carbon material can also be exposed to a vapor of Li atoms. Electrons are transferred from the metal atoms to the organic material. The lithium cations thus neutralizing the doping charges. In the process, the free energy of the reaction is not used to produce electrical energy but directly transformed into heat. The chemical intercalation method used in this work provides parameters needed to describe the carbon-based electrode in Li-ion batteries.

Up to now, the major criterion used to find organic electrode materials for Li batteries is the amount of lithium that can be intercalated in the material. High levels of Li concentration of up to about $\text{LiC}_{3.3}$ can be achieved in both, amor-

phous and polycrystalline polyaromatic hydrocarbon material,^{4,5} C_{60} ,⁶ carbon nanotubes⁷ and graphite,⁸ and even more under high pressure.⁹ In the promising poly(*para*-phenylene)-based and polyacenic semiconductor materials obtained from heat treatment of polymers, intercalation levels as high as $\text{LiC}_{\sim 2}$ are reached.^{10,11} Finite-size polyaromatic hydrocarbons are model systems for infinite graphene sheets.¹²⁻¹⁵

In the search for improved carbon-based energy storage materials, the amount of intercalated lithium is not the only parameter to be considered. Other key parameters are (i) the amount of charge transfer per carbon atom from the Li atom to the carbon material which is related to the capacity of the electrode, and (ii) the energy gain per electron transferred which determines how strong the Li ions are bound to the electrode. The product of both determines the energy gain per carbon atom, i.e., the stability of the intercalated electrode material. In contrast to the high amount of Li atoms intercalated into carbon-based films,⁴⁻⁷ the amount of charge transfer is usually hard to address. From photoelectron spectroscopy on graphite intercalation compounds (GICs) and early theoretical modeling, the Li atom was believed to be ionic.^{16,17} More recent quantum-chemical calculations suggest a lower degree of charge transfer for these LiC_6 and LiC_8 compounds.^{18,19} The modeling of complexes of lithium and organic molecules¹²⁻¹⁵ or even on dimers of molecules^{20,21} provided insight into lithium atom bonding configurations and positions with respect to the molecule. Often it is found that charge transfer from lithium atoms to the molecules is not complete.^{12-14,18,19}

Electron binding energies and formation enthalpies of

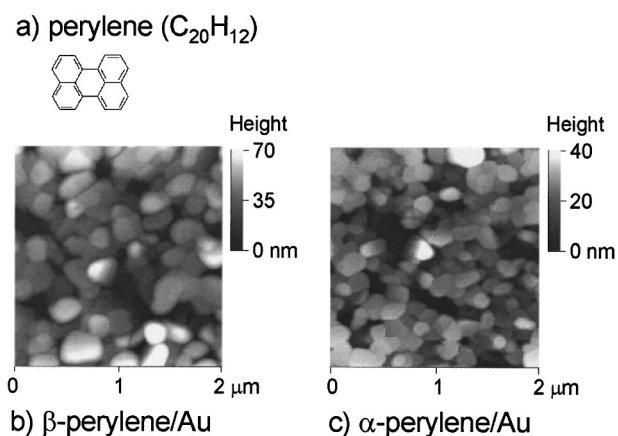


FIG. 1. (a) Sketch of the perylene molecule. TM-SFM height of (b) β -perylene and (c) α -perylene films.

isolated lithium-molecule complexes do not usually match those of the intercalated molecular solid.²² The main reason is that electronic polarization effects have to be taken into account for a proper description of solid-state equivalents. One of the major difficulties lies in determining the Madelung energy,²³ which stabilizes the formed intercalation compound, as an infinite sum of polarization-screened electrostatic interactions. Alternatively, the role of intermolecular polarization for the stabilization of charge-transfer salts can be studied experimentally using valence- and core-level photoelectron spectroscopy.²²

In this paper, we report on a study of Li compounds of polycrystalline films of α -perylene by photoelectron spectroscopy and compare to experimental data of polycrystalline β -perylene,⁵ C_{60} ,²² and graphite,^{16,24} in order to investigate the role of polarization in the stability of organic charge-transfer salts. Perylene was chosen for a specific reason: depending on the preparation conditions,⁵ the nonlinear five-ring aromatic molecule perylene ($C_{20}H_{12}$, see Fig. 1) condenses into either one of two monoclinic structural forms (space group $P2_1/a$), called α - and β -perylene.^{25,26} In the α crystal, molecules form physical dimers, in contrast to the monomeric β -crystalline form. The closer distance between the two adjacent molecules in the dimers affects the polarization energies (also called intermolecular relaxation energy) which act to screen positive (P^+) and negative (P^-) charges. P^+ of α -perylene is 0.3 eV larger than for β -perylene.⁵ Thus, the influence of the polarization energy can be studied using two structural modifications of the same material, limiting the number of parameters changed.

II. EXPERIMENT

Polycrystalline α - and β -perylene films with a thickness of 20–50 nm are prepared in ultrahigh vacuum (pressure during evaporation $<5 \times 10^{-10}$ mbar) by condensation of a perylene vapor on a cold polycrystalline gold substrate. Following established procedures, the gold substrates are held at different temperatures to obtain β -perylene (170 K) and α -perylene (230 K).⁵ During the spectroscopic measurements, the samples are kept at those temperatures. Alternatively, films of α -perylene could be made *in situ* by conver-

sion from the β phase at about 410 K in a nitrogen atmosphere at a pressure of about 1 bar. This temperature is close to that reported for the bulk phase transition.²⁵ The transition occurs within a few seconds, starting from the edges of the film, as monitored visually by a slight change of color and reflection behavior. Directly prepared and α -perylene films made by conversion had similar electronic properties, both in the pristine and intercalated case, as revealed by photoelectron spectroscopy. The spectra shown in this publication are obtained from directly prepared films.

The intercalation with Li atoms is performed *in situ* by exposing the organic films to a vapor of lithium from heated, out-gassed SAES getter sources.⁵ By the efficient use of cryo pumps, a pressure $<1 \times 10^{-10}$ mbar is maintained during and in between the exposures. Ultraviolet- (UPS) and x-ray (XPS) photoelectron spectroscopies are carried out as described elsewhere.⁵ The elemental composition of the films is derived from the intensity of the core-level lines using the Li/C cross-section ratio obtained in previous work.⁵ The amount of oxygen in the film was below the XPS detection limit, at all intercalation stages. Spectra are plotted with respect to the vacuum level (E_V), obtained by adding the work function to the binding energy defined versus the Fermi level (E_F).

The morphology of the pristine films is studied in air by tapping-mode scanning force microscopy (TM-SFM) in a Nanoscope IIIa system (Digital Instruments, Santa Barbara, CA) after warming up the samples to room temperature, at atmospheric nitrogen pressure. Both the height and phase signal are recorded with a scan rate of 0.7 lines/s and a lateral resolution of 512 pixels. Surface profiles were quantified using the NANOSCOPE software. Noncontact “golden” silicon cantilevers with a tip height of 10–20 μm and a typical curvature radius of less than 10 nm are used.

III. DATA EVALUATION USING A BORN-HABER CYCLE

Following the basic idea outlined by Schnadt *et al.*,²² photoelectron spectroscopy data are used to estimate the formation enthalpy ΔH^0 of the intercalation compounds from a Born-Haber cycle.^{18,27–29} In the cycle, the starting point is the lithium metal (with a cohesive energy of 1.6 eV per atom²³) and the perylene crystal [van der Waals cohesive energy per molecule $E_{\text{coh}}^{\text{vdW}}(\text{per})$ of about 1.4 eV (Ref. 31)]; the end of the process leads to the intercalated material, e.g., the $\text{Li}^+(\text{per})^-$ compound, where the $\text{Li}(2s)$ electron has been fully transferred. For the pristine perylene, such as for C_{60} ,²⁹ $E_{\text{coh}}^{\text{vdW}}(\text{per})$ is largely regained during the condensation step [$E_{\text{coh}}^{\text{vdW}}(\text{Li-per})$]. If the crystal structure of the pristine and intercalated material is similar, they should almost cancel each other, and van der Waals bonding energies can be neglected.

Within the Born-Haber cycle, a mixture of Li atoms and perylene molecules is condensed in a solid. After the charge transfer, the organic molecules in the solid are negatively charged, which costs $EA^{\text{solid}}(\text{per})$ for each molecule. Note that the following sign convention is adopted: A positive electron affinity corresponds to an energy stabilization upon negative charging. $EA^{\text{solid}}(\text{per})$ corresponds to the (adiabatic)

electron affinity in the intercalated solid that is larger than the affinity of a free molecule $EA^{\text{gas}}(\text{per})$ because of the addition of the polarization energy P^- . The electrons on the molecules come from the ionization of the lithium atoms [ionization potential $IP^{\text{solid}}(\text{Li})$]. The $IP^{\text{atom}}(\text{Li})$ of a free Li atom is 5.4 eV;³² but it is reduced at the site of the Li atom in the solid by a polarization energy δIP due to the screening from neighboring molecules: $IP^{\text{solid}}(\text{Li}) = IP^{\text{gas}}(\text{Li}) - \delta IP$.²² The value of the polarization energy δIP can be extracted from the $\text{Li}(1s)$ binding energy of the Li-intercalated perylene solid. Note that this is possible for two reasons: First, the polarization energy δIP for a positive charge in the $2s$ orbital is likely to be very similar to the polarization energy of a core hole in the $\text{Li}(1s)$ orbital, since both are localized compared to the perylene-lithium distance. Second, photoionization of the $\text{Li}(1s)$ level of a Li^+ ion is accompanied by a fast electron backtransfer from the organic system to the $\text{Li}(2s)$ level. Hence, the photoelectron emission experiment characterizes the singly charged Li atom [like it appears in the $\text{Li}^+(\text{per})^-$ compounds] rather than the doubly ionized Li atom.^{5,22}

In the Born-Haber cycle, finally, the electrostatic interactions in the $\text{Li}^+(\text{per})^-$ solid are “turned on,” which gives rise to a considerable stabilization energy, the Madelung energy M .²³ The total enthalpy gain per molecule ΔH^0 for the chemical or electrochemical intercalation process is³⁶

$$\Delta H^0 = E_{\text{coh}}(\text{Li}) + IP^{\text{atom}}(\text{Li}) - \delta IP - EA^{\text{solid}}(\text{per}) - M. \quad (1)$$

An explicit, albeit difficult calculation of M and the estimate of $EA^{\text{solid}}(\text{per})$ can essentially be avoided by using data obtained by photoelectron spectroscopy.²² The sum of M and EA^{solid} equals the electron affinity of a molecule in the intercalated solid, which is accessible via inverse photoemission spectroscopy.^{33,34} Alternatively, the affinity of the intercalated system is estimated by the low-binding energy onset E_B^* of the new valence peaks that appear in the UPS spectrum upon intercalation.²² This approximation is reasonable as long as the (single-particle) electronic gap in the intercalated system is vanishingly small, such as in C_{60} and graphite.^{34,35} This situation is assumed for the Li-perylene systems.³⁰

The formation enthalpy per molecule ΔH^0 of the intercalated compounds is estimated by the final expression

$$\Delta H^0 = E_{\text{coh}}(\text{Li}) + IP^{\text{atom}}(\text{Li}) - \delta IP - E_B^*. \quad (2)$$

Similar estimates can be done for several charges transferred. In this case, the corresponding affinity and Madelung values for the second, third, etc., electron must be considered.

IV. RESULTS AND DISCUSSION

A. Experimental results

The TM-SFM images of the β - and α -perylene films are shown in Figs. 1(b) and 1(c), respectively. Both films have an identical morphology. The grain size has a rather narrow distribution with diameters between about 150 and 250 nm. The grains might correspond to single-domain crystallites.

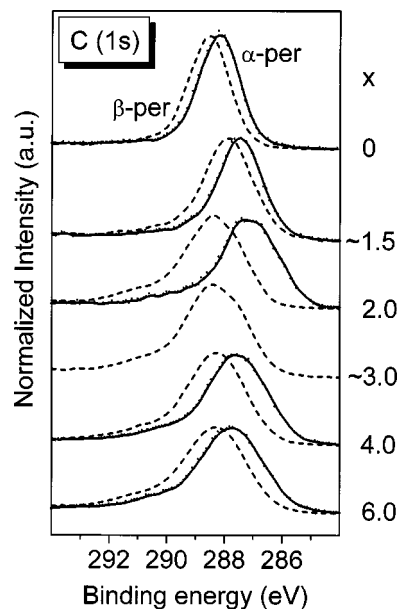


FIG. 2. $\text{C}(1s)$ XPS spectra of Li compounds of β - and α -perylene at various intercalation levels x .

Clearly, differences in the photoelectron spectra of the two films are then not related to the macroscopic morphology but rather to differences in the local aggregation state.

Intercalation of α -perylene films results in the formation of stoichiometric compounds $\text{Li}_x(\text{perylene})$ with $x=2, 4$, and 6 (all ± 0.2), similar to β crystalline and amorphous perylene films.⁵ Similar stoichiometries are obtained in a large number of experiments.

The $\text{C}(1s)$ core-level spectra of pristine and intercalated α - and β -perylene films are shown in Fig. 2. Between pristine α - and β -perylene, the difference in the $\text{C}(1s)$ core-level binding energies is similar to the difference in the threshold ionization potential, IP^{solid} , of about 0.3 eV, indicating that P^+ is the same for both electronic levels. At low x , for both α - and β -perylene, the $\text{C}(1s)$ line shifts strongly towards lower binding energy upon intercalation. The evolution of the position of the peak maxima as a function of x is displayed in the upper part of Fig. 3. For the β -crystalline form at low x , the shift amounts to about 0.6 eV and ends at an intercalation level *below* two Li atoms per molecule (at $x \approx 1.5$). At higher levels ($x \geq 2$), the $\text{C}(1s)$ peak of the Li-intercalated β crystal turns back to higher binding energies, while for α -perylene, the $\text{C}(1s)$ line continues to shift, 1.0 eV in total, up to a level of *at least* two Li atoms per molecule. Two observations are pinpointed.

(i) A chemical shift of the $\text{C}(1s)$ core level correlates to the amount of charge transferred from Li atoms to the π system. Since the shift of the $\text{C}(1s)$ line is linear with the intercalation level x up to a level of $x=2$, the amount of charge transferred is two electrons per molecule in α -perylene at this level, if one assumes a complete charge transfer at lowest x . This is not achievable for β -perylene, as indicated by the smaller shift.

(ii) At high x , the intercalated α - and β -perylene films have different electronic properties. This suggests that dimer-

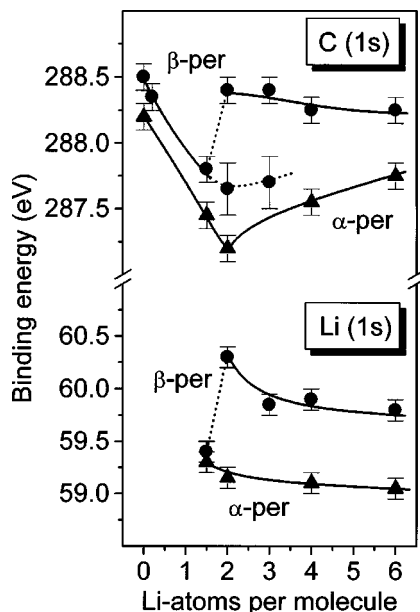


FIG. 3. The C(1s) and Li(1s) binding energies of Li compounds of β - and α -perylene at various intercalation levels x .

ization in the bulk of α -perylene is maintained at high intercalation levels.

At intercalation levels $x < 2$, two new features appear in the UPS spectra (A and B in Fig. 4) for both α - and β -perylene, at the low-binding energy side of the former highest occupied molecular orbital (HOMO). Since the amount of oxygen in the films is negligible, electronic states related to oxygen containing species should be ruled out. The similarity in the shape of the spectra for the two $\text{Li}_x(\text{perylene})$ systems, at $x \sim 1.5$, indicate that both intercalated films are rather similar in the surface region probed by UPS (of less than about 10 Å). The peak derived from the former HOMO splits into two features with binding energies close to those of the HOMO of the pristine α and β form, of about 5.2 and 5.5 eV.⁵ This provides an evidence that the first and possibly the second molecular layers contain both the monomeric and dimeric forms. Peak A and B are split by the same amount. These two spectral features originate from the same electronic state—the partially filled lowest unoccupied molecular orbital (LUMO) stabilized by the Li counterion—but experience a different polarization energy: P^+ for A (creation of the photohole on the site of a dimer) is higher than that for B (hole on a monomer).

At $x \geq 2$, the valence spectra are similar in shape but the spectrum of the intercalated original α film appears shifted by 0.4–0.6 eV towards lower binding energies. For high intercalation levels, only either the monomeric or the dimeric structure is present in the surface region of the film, confirming the interpretation obtained from the C(1s) spectra about a presence of a dimeric structure in Li-intercalated α -perylene films at $x \geq 2$. Such a behavior can only occur, if, after diffusion of lithium ions from the surface to the bulk, the bulk stays either α or β crystalline, and serves as a template for the structural reorganization of the surface at higher x . That is, the appearance of double features at low x is a surface phenomenon, and the onset values of $E_B^* = 2.7$ eV for

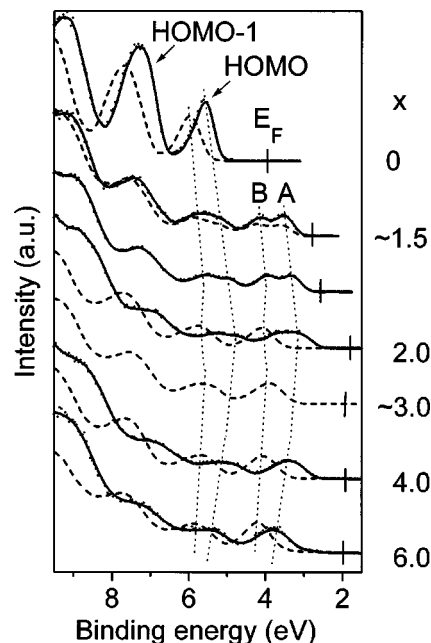


FIG. 4. UPS valence spectra of pristine and Li-intercalated, polycrystalline β - (from Ref. 5) and α -perylene films on gold substrates. The position of the spectrometer Fermi level (E_F) is indicated by a vertical mark for each spectrum. Features A and B appear upon intercalation.

feature A and of $E_B^* = 3.7$ eV for feature B represent the lowest electron binding energies at $x = 2$ in the bulk of the intercalated α (feature A) and β material (feature B), respectively.

The Li(1s) core-level spectra of the intercalated films are shown in Fig. 5. The evolution of the position of the peak maxima with increasing x is displayed in Fig. 3. For the dimeric system, for $x < 2$, the Li(1s) binding energy $E_B^{\text{Li}(1s)}$ of 59.4–59.8 eV is close to the value for β perylene and stage-1 GIC. At higher levels, $x \geq 2$, the peak position shifts with x towards lower binding energy, up to 1 eV lower than

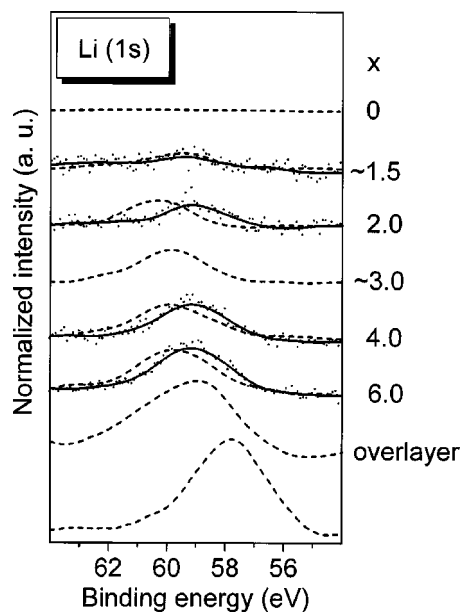


FIG. 5. Li(1s) XPS spectra of Li compounds of β - (from Ref. 5) and α -perylene at various intercalation levels x .

TABLE I. Formation enthalpies of Li-intercalation compounds of C_{60} , graphite, α - and β -perylene derived from experimentally obtained values for the $Li(1s)$ binding energies, $E_B^{Li(1s)}$, the binding energy of the least bound electron, E_B^* . The Madelung energy M can be obtained from the electron affinity of the pristine material, EA^{solid} , and E_B^* . The spread in E_B^* corresponds to the positions of two features in the C_{60} system and to a broad structure in stage-1 GIC.

	$E_B^{Li(1s)}$ (eV)	E_B^* (eV)	EA^{solid} (eV)	δIP (Li) (eV)	IP^{solid} (Li) (eV)	M (eV)	$-\Delta H^0$ per charge and molecule (eV)	$-\Delta H^0$ per charge and carbon atom (eV)	$-\Delta H^0$ (Wh/kg)
C_{60}	61.8 ^a	5.1 -5.6 ^a	3.5 ^b	2.7	2.7	1.6 -2.1	0.8-1.3	0.013 -0.022	36±10 (first charge)
Graphite LiC_6	59.4 ^c	2.8 -3.3 ^c		4.6	0.8				109 ± 43 (for 0.5 charges per Li atom)
β -perylene ($x=2$)	60.2 ^d	3.7 ^d		4.3	1.1		1.0	0.050	171±30 (for 1.5 charges)
α -perylene ($x=2$)	59.2	2.7	2.5 ^e	5.3	0.1	0.2	1.0	0.050	228±30 (for 2 charges)

^aUsing the experimental values from Ref. 22.

^bReference 37.

^cReference 16, using the work function from Ref. 24.

^dReference 5.

^eReferences 38 and 39.

for intercalated β -perylene. For $x \geq 2$ in α -perylene, holes at the Li sites are better screened than in the monomeric β -perylene system, as indicated by the 1 eV energy shift of the $Li(1s)$ line. Correspondingly, ionizing a Li atom in an α -perylene environment is easier than in a β -perylene crystal.

B. The role of electronic polarization

Table I displays the formation enthalpy ΔH^0 calculated from Eq. (3) for the following intercalated systems: Li_xC_{60} for $x=1$ [using literature experimental electron spectroscopy data for the compound with a nominal level of $x < 1$ (Refs. 22, and 37) and assuming full charge transfer], the stage-1 graphite intercalation compound LiC_6 (binding energies from Refs. 16 and 24) for a charge transfer of 0.5 electrons per Li atom,¹⁹ and for the $Li_2(\beta\text{-per})$ systems. For the last systems, the charge transfer is different, as indicated by the $C(1s)$ chemical shift. For the calculations of ΔH^0 , we use the amount of 1.5 charges for $Li_2(\beta\text{-per})$ and 2 charges for $Li_2(\alpha\text{-per})$.

Measured electron binding energies E_B^* are rather similar for graphite and α -perylene, but 0.4–0.9 and 2.4–2.9 eV higher in the β -perylene and C_{60} compounds, respectively. The value of δIP is also different for these four materials. In particular, at the tetrahedral site within the fcc lattice of C_{60} (Ref. 22) it is much lower than that in the solids of the planar molecules and graphite. It can be recognized that the difference in δIP is opposite to that in E_B^* . The sum ($\delta IP + E_B^*$) in Eq. (1) is rather similar in all of these systems. In other words, this means that a higher polarizability reduces the Madelung energy but increases the electron-accepting capa-

bility of the organic system and facilitates the ionization of lithium atoms in the molecular solid environment. As a result, ΔH^0 per transferred charge and molecule is also of the same magnitude (–0.8 to –1.3 eV).

The magnitude of M (for the first transferred charge) can be evaluated from the experimental values of E_B^* and EA^{solid} . $M = E_B^* - EA^{solid}$ (according to the assumptions discussed in Sec. III). Using $EA^{solid}(C_{60}) = 3.5$ eV,³⁷ M is 1.6–2.1 eV for LiC_{60} . Note that this is only slightly smaller than the unscreened value (2.3 eV) calculated for a Li ion at the tetrahedral site of the C_{60} fcc lattice.²² For the Li compound of α -perylene, M amounts to only about 0.2 eV, much smaller than the value obtained for LiC_{60} . This is unexpected because the unscreened M is inversely proportional to the lattice constant²³ and the Li-perylene solid has a smaller average distance between positive and negative ions than the fullerite. The low value of M suggests the efficient screening of electrostatic interactions in the α -perylene solid.

C. Degree of charge transfer and limitations in the electrode capacity

According to Table I, for both $Li_2(\alpha\text{-per})$ and $Li_2(\beta\text{-per})$, the formation enthalpy ΔH^0 per charge and molecule is about –1.0 eV. For perylene, the LUMO is not degenerate. The next unoccupied orbital (LUMO+1) is about 1.3 eV higher in energy.³⁸ This amount of energy is too large to add a third charge, in agreement with the observation from the chemical shift of the $C(1s)$ core-level line in α -perylene, which stops at about $x=2$. In this system, the amount of total electron transfer to the π system seems to be limited by the spacing of unoccupied electronic levels. A

negative formation enthalpy per mass of 228 ± 30 Wh/kg is obtained. This value is more than double of that in the stage-1 lithium graphite intercalation compound (LiC_6) if the charge transfer would be only about 0.5 charge per Li atom.¹⁹

For β -perylene, the total amount of charge transfer (of about 1.5 electrons) and therefore also the charge capacity is even lower than in α -perylene, resulting in a negative formation enthalpy ΔH^0 per charge and molecule equal to only 171 ± 30 Wh/kg. The lower degree of total charge transfer, and therefore of the lower capacity, might be related to the higher $\text{IP}^{\text{solid}}(\text{Li})$ of a lithium atom in the β -perylene environment. On the other hand, the polarization energy P^+ at the site of the molecules (monomeric configuration) remains basically the same as demonstrated by the unaffected binding energies of the β -derived original valence band features, e.g., of the peaks denoted as HOMO and HOMO-1, upon intercalation. It can be concluded that the local environment of the Li atoms has changed, possibly due to the formation of Li dimers.

In general, for perylene at low x , the charge transfer seems to be complete and the Li-molecule bond is ionic. At higher intercalation levels, although more lithium atoms are incorporated into the solid, the total charge transferred to the molecules saturates. This translates into a more covalent character of the bond between the Li atoms and the negatively charged molecule. The transition from the ionic to the covalent character of the bond between the Li atom(s) and perylene upon intercalation can be understood from the reduction of the energy difference of the orbitals involved ($2s$ of lithium and und the unoccupied of perylene) following the negative charging of perylene.

V. CONCLUSIONS

Valence- and core-level photoelectron spectroscopies are used to characterize the bonding configuration of the alkali metal atoms and to determine the amount of charge transfer in Li-intercalation compounds of the polyaromatic hydrocarbon perylene. The formation enthalpy of these compounds is evaluated from a Born-Haber cycle and a direct use of spectroscopic data. For polycrystalline solids of perylene, it is found that the negative formation enthalpy is not proportional to the number of Li atoms in the intercalation compounds, because at higher intercalation levels, the charge transfer per Li atom is only partial. The maximal amount of charge transfer is limited by different phenomena according to the type of crystal: (i) the availability of energetically favorable unoccupied electronic levels, in α -perylene, or (ii) the magnitude of the intermolecular polarization energy for the positive charge at the site of the Li atom, in β -perylene.

Intermolecular polarization is found to have only a minor influence on the formation enthalpy per charge and molecule. This is because the effect of intermolecular polarization on the ionization potential of Li atoms, and on the electron-accepting capability of molecules, is compensated by a screening of the Madelung energy. On the other hand, it influences the amount of total achievable charge transfer because it facilitates the ionization of lithium atoms in the molecular solid environment. A search for better organic elec-

trode materials should therefore also include the consideration of the polarization energies in the solid (which can be influenced by the choice of the aggregation state).

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¹G. Pistoia, *Lithium Batteries* (Elsevier, Amsterdam, 1994).

²D. R. Sadoway and A. M. Mayes, *MRS Bull.* **27**, 591 (2002).

³J.-M. Tarascon and M. Armand, *Nature (London)* **414**, 359 (2001).

⁴M. Keil, P. Samorì, D. A. dos Santos *et al.*, *J. Chem. Phys.* **116**, 10854 (2002).

⁵R. Friedlein, X. Crispin, M. Pickholz, M. Keil, S. Stafström, and W. R. Salaneck, *Chem. Phys. Lett.* **354**, 398 (2002).

⁶L. Cristofolini, M. Ricco, and R. de Renzi, *Phys. Rev. B* **59**, 8343 (1999).

⁷H. Shimoda, B. Gao, X. P. Tang, A. Kleinhammes, L. Fleming, Y. Wu, and O. Zhou, *Phys. Rev. Lett.* **88**, 015502/1 (2002).

⁸J. E. Fisher and T. E. Thompson, *Phys. Today* **36** (1978).

⁹V. A. Nalimova, D. Guerard, M. Lelaurain, and O. V. Fateev, *Carbon* **33**, 177 (1995).

¹⁰S. Yata, H. Kinoshita, M. Komori, N. Ando, T. Kashiwamura, and T. Harada, *Synth. Met.* **62**, 153 (1994).

¹¹K. Sato, M. Noguchi, A. Demachi, N. Oki, and M. Endo, *Science* **264**, 556 (1994).

¹²H. Ago, M. Kato, K. Yahara, K. Yoshizawa, K. Tanaka, and T. Yamabe, *J. Electrochem. Soc.* **146**, 1262 (1999).

¹³D. A. Morton-Blake, J. Corish, and F. Bénére, *Theor. Chim. Acta* **68**, 389 (1985).

¹⁴M. Nakadaira, R. Saito, T. Kimura, G. Dresselhaus, and M. S. Dresselhaus, *J. Mater. Res.* **12**, 1367 (1997).

¹⁵M. Yagi, R. Saito, T. Kimura, G. Dresselhaus, and M. S. Dresselhaus, *J. Mater. Res.* **14**, 3799 (1999).

¹⁶W. Eberhardt, I. T. McGovern, E. W. Plummer, and J. E. Fisher, *Phys. Rev. Lett.* **44**, 200 (1980).

¹⁷S. Rabii, J. Chomelier, and G. Loupiau, *Phys. Rev. B* **40**, 10105 (1989).

¹⁸S. Doyen-Lang, A. Charlier, L. Lang, M. F. Charlier, and E. McRae, *Synth. Met.* **58**, 95 (1993).

¹⁹C. Hartwigsen, W. Witschel, and E. Spohr, *Phys. Rev. B* **55**, 4953 (1997).

²⁰L. G. Scanlon and G. Sandi, *J. Power Sources* **81–82**, 176 (1999).

²¹A. Crispin, X. Crispin, M. Fahlman *et al.*, *J. Chem. Phys.* **116**, 8159 (2002).

²²J. Schnadt, P. A. Brühwiler, N. Mårtensson, A. Lassesson, F. Rohmund, and E. E. B. Campbell, *Phys. Rev. B* **62**, 4253 (2000).

²³C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976).

²⁴G. K. Wertheim, P. M. T. M. V. Attekum, and S. Basu, *Solid State Commun.* **33**, 1127 (1980).

²⁵E. von Freyendorf, J. Kinder, and M. E. Michel-Beyerle, *Chem. Phys.* **27**, 199 (1978).

²⁶J. Tanaka, *Bull. Chem. Soc. Jpn.* **36**, 1237 (1963).

²⁷R. M. Metzger, *Mol. Cryst. Liq. Cryst.* **85**, 97 (1982).

²⁸L.-S. Wang, O. Cheshnovsky, R. E. Smalley, J. P. Carpenter, and S. J. Wu, *J. Chem. Phys.* **96**, 4028 (1992).

²⁹Y. Wang, D. Tománek, G. F. Bertsch, and R. S. Ruoff, *Phys. Rev. B* **47**, 6711 (1993).

³⁰An upper limit for the gap in the intercalated material is given by the difference between $E_{\text{A}}^{\text{solid}}$ of the pristine material and E_{B}^* (that is if M is

zero), estimated for the lithium α -perylene system at $x=2$ to be about 0.2 eV.

- ³¹The van der Waals cohesive energy $E_{\text{coh}}^{\text{vdW}}$ (per) equals the heat of sublimation which can be obtained from the temperature dependence of the saturated vapor pressure [M. Stephenson and S. Malanowski, *Handbook of the Thermodynamics of Organic Compounds* (Elsevier, New York, 1987)] using the van't Hoff equation [R. T. Grimley, *The Characterization of High-Temperature Vapors* (Wiley, New York, 1967)].
- ³²R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Los Angeles, 1981).
- ³³J. L. Martins and N. Trouiller, *Phys. Rev. B* **46**, 1766 (1992).
- ³⁴P. J. Benning, D. M. Poirier, T. R. Ohno *et al.*, *Phys. Rev. B* **45**, 6899 (1992).
- ³⁵C. S. Fadley, in *Electron Spectroscopy: Theory, Techniques, and Applications*, edited by C. R. Brundle and A. D. Baker (Academic, London, 1978).
- ³⁶Since the beginning and the end of the cycle only concern solids, all entropy change upon intercalation is neglected since entropic terms are expected to cancel each other significantly over the cycle. This assumption allows us to describe the cycle in terms of enthalpies.
- ³⁷C. Gu, D. M. Poirier, M. B. Jost, P. J. Benning, Y. Chen, T. R. Ohno, J. L. Martins, and J. H. Weaver, *Phys. Rev. B* **45**, 6348 (1992).
- ³⁸K. H. Frank, P. Yannoulis, R. Dudde, and E. E. Koch, *J. Chem. Phys.* **89**, 7569 (1988).
- ³⁹V. V. Aleksandrov, A. I. Belkind, I. Y. Muzikante, E. A. Silinsh, and L. F. Taure, *Sov. Phys. Solid State* **18**, 1405 (1976).