Molecular parameters controlling the energy storage capability of lithium polyaromatic hydrocarbon intercalation compounds

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Abstract

One route for improving the performance of Li-based batteries is to optimize the carbon-based electrode. In order to find the best carbon-based materials, the specific roles of the molecular and solid-state contributions have to be understood. Here, the molecular contributions are analyzed. A semi-quantitative method is proposed to compare the charge storage capability of polyaromatic hydrocarbon molecules (PAHs). For planar PAHs, the ability to store electrical energy is found to be to a large extend determined by a single parameter, that is the electronic hardness (half the electronic gap) multiplied the number of carbon atom in the molecule. A compilation of results for oligophenyls, oligoacenes and medium-size planar systems suggests trends in the dependence of the energy storage capability on the size and shape of the molecules.

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1. Introduction

Lithium-ion and Li-metal batteries using carbon-based electrodes are state-of-the-art high performance power sources [1–4]. The low standard electrode potential of lithium metal (≈ -3.05 V) and the small size of the lithium ions (≈ 0.6 Å) grant high-energy densities and re-chargability of the batteries; thus making them appropriate for portable applications.

One route to improve the performance of Li-based batteries is to optimize the carbon electrode material that is intercalated with lithium ions upon charging (Li-ion battery) or discharge (Li-metal battery) of the device. This might be achieved by a better understanding of the fundamental mechanisms and the energetics underlying the intercalation process. For Li-metal batteries, in particular, the two key parameters are: firstly the amount of charge stored per carbon atom; secondly, the energy gain per charge. The product of both determines the energy gain per carbon atom, thus the total gravimetric energy density.

High levels of Li-intercalation, up to about $LiC_{3.3}$, is achieved in both, amorphous and polycrystalline polyaromatic hydrocarbon (PAH) materials [5–9], C_{60} [10], carbon nanotubes [11] and graphite [12]. For poly(p-phenylene)-based, as well as polyacenic semiconductor (PAS) materials obtained from high-temperature treatment of polymers, intercalation levels as high as $LiC_{\sim 2}$ are reached [6–13]. In contrast to the amount of Li-atoms intercalated, the amount of charge transferred is usually hard to address. Recent quantum-chemical calculations suggest an incomplete charge transfer for the LiC_6 and LiC_8 graphite intercalation compounds [14,15] as well as for lithium complexes of smaller polyaromatic hydrocarbons [16–19] or even on molecular dimers [20,21].

The energy stored per transferred electron is best described by the formation enthalpy ΔH° of the intercalation compound. The formation enthalpy of an isolated Li-molecule complex obtained from quantum chemical calculations does not match directly that of the intercalated molecular solid [9,22,23]. An accurate estimate of the formation enthalpy of the Li-molecule intercalation material must take into account electronic polarization effects screening the electrostatic interactions. The electronic polarization characterizes the deformation of the electron density as a response to an (external) electric field [24]. One of the major difficulties lies in determining the Madelung energy as an infinite sum of polarization-screened electrostatic interactions between positive and negative charges. Recently it was found that photoelectron spectroscopy gives many information on the lithium intercalation [9,23]: the electronic configuration of the Li-atoms in organic solids, the formation enthalpy via the Born–Haber cycle, the role

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of the electronic polarization present for various molecular crystalline phases, and even a first estimate of the (polarization-screened) Madelung energy.

In the present paper, we identify the relevant molecular parameters for the electron-accepting capability of molecules in battery applications. Those molecular parameters (electron affinity, chemical hardness) are normalized to the number of carbon atoms in the molecule, or alternatively to the mass since energy densities are required to compare various organic solids.

2. Results and discussion

2.1. The molecular electron affinity

The ability of a molecule to accept an electron is determined by the electron affinity. The adiabatic electron affinity (EA) of a free molecule is defined in terms of the total energy difference between the lowest vibrational state of the neutral molecule and the lowest vibrational state of the singly negatively charged molecule. The vertical electron affinity is the energy difference between the neutral and negatively charged molecule that has the structure of the neutral molecule in the ground state. Differences between the adiabatic and vertical affinities are typically of the order of 0.1–0.2 eV [25,26].

Density functional theory (DFT) provides an expression of the total energy of a molecule as a function of the number of added electrons. The total energy of a negatively charged molecule $E^{\text{tot}}(x)$, carrying a charge x, can be expressed from the total energy $E^{\text{tot}}(x = 0)$ of the neutral molecule via a Taylor series [27–29]:

$$E^{\text{tot}}(N = N_0 - x) = E^{\text{tot}}(x = 0) - x \left(\frac{\partial E^{\text{tot}}}{\partial N} \right)_{N=N_0}$$
$$+ \left(\frac{x^2}{2} \right) \left(\frac{\partial^2 E^{\text{tot}}}{\partial N^2} \right)_{N=N_0} - R(x^3) \qquad (1)$$

where $R(x^3)$ represents the higher-order terms of the series. N_0 stands for the number of electrons in the neutral and N is the charged molecule. The higher-order terms are expected to be small, as found for Cu-clusters [29] and for the C_{60} molecule [30]. The total energy of the charged molecule is then a quadratic function of the charge state x as shown for C_{60}. Note that small discontinuities occur only after filling of shells. Eq. (1) is quantitatively valid for x between -1 and 1. Hence, its use for higher doping levels provides only a qualitative tool to compare PAHs molecules. For non-integer charge, Eq. (1) does not have a physical meaning for isolated molecules, although it can be used for open-systems [31] and eventually molecular solids with a possible partial charge transfer from alkali metal atoms to the molecular π-system. The advantage of using this formula for non-integer charges is to provide a method to compare the charge storage ability of various molecules for a certain gravimetric charge density.

In DFT, the first derivative of the expansion, $(\partial E / \partial N)_{N=N_0}$, considering charge addition, is defined as the chemical potential μ of the electronic system. Like in thermodynamics, the chemical potential expresses how the energy changes with the number of particles in the system [32]. The chemical potential can be seen as the global electronegativity for a molecule. Indeed, in the finite difference approximation, it is estimated to be the opposite of the average between the ionization potential and the electron affinity [29,33]:

$$\mu \approx -\tfrac{1}{2}(\text{IP} + \text{EA}), \qquad \eta \approx \tfrac{1}{2}(\text{IP} + \text{EA}) \qquad (2)$$

which is nothing but the Mulliken electronegativity for atoms [34]. Half of the second derivative, $(1/2)\,(\partial^2 E^{\text{tot}}/\partial N^2)_{N=N_0}$, defines the absolute hardness η of the electronic cloud of a molecule (η is always positive) [33]. The nonchemical meaning of the word "hardness" is resistance to deformation or change. In DFT, hardness can be regarded as the resistance of the chemical potential to a change in the number of electrons [33]. It is also related to the static dipole polarizability, α [35–37]. In the finite difference approximation, the hardness is half the difference between the ionization potential and the electron affinity (Eq. (2)).

Eq. (2) is used to calculate μ and η from the experimental values of IP and EA for a number of polyaromatic hydrocarbon molecules and oligophenyls (Table 1). According to Eq. (1), the electron affinity of a molecule, a central parameter in the determination of formation enthalpy of intercalated compounds (Eq. (2)), can be written in terms of μ and η:

$$\text{EA} = \mu + \eta \qquad (3)$$

Since the chemical potential is similar (about 4 eV) for most polyaromatic hydrocarbon molecules [38,39] (except for the fullerene C_{60}), the electron affinity variation among those molecules is directly related to a change in chemical hardness. A significant decrease in η is observed when increasing the size of the molecular π-system (Table 1).
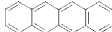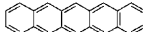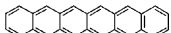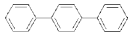
According to Eq. (2), η appears to be half of the electronic gap of a molecule. Consequently, the larger the conjugated molecule, the smaller the electronic gap, the smaller the hardness and the more polarizable the electronic cloud [61]. As expected, larger molecules are softer; that is, it is easier to charge those molecules with the first electron.

2.2. Optimal electron-accepting molecular π-systems

For energy storage applications, the gravimetric energy density is the relevant property of a solid. Among the polyaromatic hydrocarbons, the energy storage capability of each molecule has to be compared for the same gravimetric charge density, i.e. for the same number of charge per carbon atom (neglecting the weight of the hydrogen atoms). The total energy change upon charging the molecule can be divided by the number of carbon atoms, N_C, in the molecule. Since

Table 1

Experimental values of the gas phase (vertical) electron affinity and (vertical) ionization potential IP^{gas} of some polyaromatic hydrocarbon molecules and oligophenyls obtained from electron capture detector (ECD) or photoelectron spectroscopy (PES) measurements, the molecular electronic hardness η, and the energy cost for -0.1 charge per carbon atom, ΔE^{tot} ($x/N_C = -0.1$), according to Eq. (4)

Molecule			Electron affinity and ionization potential		Chemical potential and electronic hardness			Energy cost for $-0.1|e|$/C-atom
Name	Chemical structure	N_C	EA^{gas} (eV)	IP^{gas} (eV)	$-\mu$ (eV)	η (eV)	$N_C\eta$ (eV)	$\Delta E^{tot}/N_C$ ($x/N_C = -0.1$) (eV)
Benzene		6	-1.12 [40] -1.15 [41]	9.24 [42] 9.25 [43]	4.06 ± 0.02	5.19 ± 0.01	31.1	-0.09
Naphtalene		10	0.15 [44,45] 0.19 [40] 0.20 [41]	8.15 [42] 8.12 [43]	4.15 ± 0.10	3.98 ± 0.02	39.8	-0.02
Anthracene		14	0.55 [25,44–46]	7.40 [42] 7.42 [47] 7.47 [48]	3.99 ± 0.04	3.44 ± 0.04	48.2	0.08
Tetracene (naphtacene)		18	1.15 [44,45] 1.03 [46]	7.01 [42] 7.04 [48]	4.06 ± 0.04	2.97 ± 0.04	53.5	0.13
Pentacene		22	1.31 [46] 1.19 [49]	6.64 [42] 6.61 [50] 6.74 [48]	3.97 ± 0.06	2.72 ± 0.06	59.8	0.20
Hexacene		26	1.58 (theoretical value from Ref. [39])	6.44 (Ref. [26]; some results from other work cited therin)	≈ 4.0	≈ 2.4	62.6	0.22
Pyrene		16	0.59 [44]	7.41 (Ref. [26]; some results from other work cited therin)	≈ 4.0	≈ 3.4	54.4	0.14
Perylene		20	0.98 [51,52]	7.0 [53]	≈ 4.0	≈ 3.0	60.0	0.20
Coronene		26	0.54 [49]	7.25 (Ref. [26]; some results from other work cited therin)	≈ 3.9	≈ 3.4	88.4	0.49
Fullerene C$_{60}$		60	2.8 [54] 2.65 [57]	7.6 [55,56]	5.16 ± 0.07	2.44 ± 0.04	146.4	0.95
Biphenyl		12	0.13 [58]	8.34 [59]	≈ 4.2	≈ 4.1	49.2	0.07
p-terphenyl		18	0.27 (theoretical value from Ref. [39])	7.9 (Ref. [26]; some results from other work cited therin) 8.20 [60]	4.16 ± 0.10	3.89 ± 0.08	70.0	0.28

higher than quadratic terms in Eq. (1) are negligible, the energy change per carbon atom is then:

$$\frac{\Delta E^{tot}(x)}{N_C} = \frac{E^{tot}(N=N_0-x) - E^{tot}(N_0)}{N_C}$$
$$= -\mu\left(\frac{x}{N_C}\right) + N_C\eta\left(\frac{x}{N_C}\right)^2 \qquad (4)$$

with x/N_C as the variable. This expression provides the energy cost per carbon atom for a fixed number of charges per carbon atom, x/N_C. Since the chemical potential is similar for planar PAHs, the product $N_C\eta$ determines the ability of the molecule to store energy.

Table 1 displays the molecular parameter $N_C\eta$ and the energy cost to charge the molecules with 0.1 electron per carbon atom. At this charging level, energy is gained by charging the benzene and naphtalene molecules; while it costs energy for the other molecules. Molecular systems with small $N_C\eta$ require less energy to reach the same degree of charging. $N_C\eta$ appears thus as the relevant parameter to describe the energy storage capability of planar polyaromatic hydrocarbons; and it is plotted in Fig. 1 as a function of the size of the molecule, N_C.

Several trends can be recognized:

(1) The cost to charge small π-conjugated systems is lower than for large molecules at the same doping level ($x|e|/N_C$). Oligomers are favored versus polymers.
(2) Linearly fused aromatic systems (acenes) need less energy to become charged as compared to non-linearly fused, more 2D-like molecules.
(3) Among the molecules considered, the oligophenyls have the worst electron-accepting properties. In the series from benzene to *p*-terphenyl $N_C\eta$ increases linearly with the length of the chain.
(4) In contrast to the excellent ability to attract a single charge, the fullerene C_{60} might not be preferential for energy storage applications, where the amount of charge per atom matters.
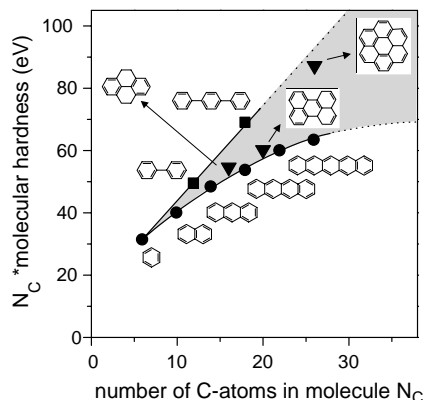

Fig. 1. The product of the molecular electronic hardness η and the number of carbon atoms in the molecule N_C of acenes (full circles), non-linear polyaromatic hydrocarbon molecules (open triangle) and oligophenyls (full squares) as a function of N_C are shown. Lines are guides for the eye.

3. Outlook

A semi-quantitative method is proposed to compare the energy storage ability of various polyaromatic hydrocarbon molecules at low-charging levels. The energy storage in molecules is discussed in terms of two global electronic properties defined in density functional theory: the chemical potential and the absolute hardness. Since planar PAHs have similar chemical potentials, the absolute hardness multiplied by the number of carbon atoms in the molecule appears to be the relevant molecular parameter to determine the energy storage in molecules.

Evidence is presented that small- and medium-size polyaromatic and phenyl-based systems, or eventually networks thereof, might have the highest energy storage ability among all pure-carbon systems. This statement is motivated by the lower energy cost to charge those molecules for a fixed number of charge per carbon atoms. More specifically, for a given (gravimetric) charge density, linearly fused aromatic systems (oligoacenes) are preferred versus non-linearly fused, more graphene-like molecules and the oligo- or polyphenyls.

To be able to extrapolate safely the conclusions obtained for molecules to the actual Li-PAHs intercalated solids, Madelung energy, intermolecular relaxation and electronic polarization energies should also be taken into account; this will be the aim of a future work. However, the observation that small π-conjugated molecules need less energy to be charged at a defined number of charge per carbon atom is in agreement with their high level of energy storage measured experimentally [9,24].

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