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Effect of carbon mass fraction on the quantum capacitance of two-dimensional graphene/$LiCoO_2$

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Two-dimensional films based on graphene and lithium cobalt oxide are promising materials for developing efficient supercapacitor electrodes. Using density functional theory, it was shown that increasing the mass fraction of carbon in the composite reduces the quantum capacitance and specific charge at the operating potential limits of the ionic liquid electrolyte. The study assessed charge redistribution using the Mulliken, Voronoi, and Hirshfield methods, leading to conclusions on the applicability of these methods to the systems under study.

Keywords: graphene, $LiCoO_2$, quantum capacitance, charge analysis.

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Introduction

Chemical current sources capable of rapid energy exchange with powered and charging systems are critically important components for the development of today's society [1–3]. A key scientific task in this area is the development of durable and efficient electrode materials for various ion batteries and supercapacitors. Recently, a composite based on graphene and lithium-cobalt(III) oxide $LiCoO_2$ (LCO) has attracted the attention of researchers. This material retains high energy density and theoretical capacitance characteristic of LCO, while graphene provides mechanical stability and high ionic conductivity. Thus, the synergy between graphene and LCO significantly increases the overall performance of the battery, its load capacity and cycling stability [4–6]. The use of a thin-film LCO structure on graphene represents a strategically important architectural innovation compared to bulk cathode materials. This design minimizes the Li^+ diffusion path to the nanoscale and ensures full utilization of the active material volume.

According to modern concepts, the total capacity of the electrode material is the sum of Faraday and non-Faraday components [7–9]. The Faraday component includes the theoretical capacity C_F connected in parallel, determined by Faraday's law, as well as the pseudo-capacity C_{PS}, based on rapid reversible oxidation-reduction reactions. The non-Faraday component implies an electrostatic charging method and is determined through the capacity of C_{EDLS} double layer and C_Q quantum capacity, which are connected in series. Thus, in general case, the full capacity of the electrode material may be found as:

$$C_T = C_F + C_{PS} + \left(\frac{1}{C_Q} + \frac{1}{C_{EDLS}}\right)^{-1}. \qquad (1)$$

If the charge of the electrode occurs without a change in composition, as, for example, in supercapacitors, then there is no Faraday component, and the formula (1) takes the form:

$$\frac{1}{C_T} = \frac{1}{C_Q} + \frac{1}{C_{EDLS}}. \qquad (2)$$

Thus, the first-principles calculation of the quantum capacitance of electrode materials with various topologies is an important factor in the development of the chemical power sources sector. In this paper, it is planned to numerically estimate the quantum capacitance and specific charge of a two-dimensional graphene/LCO (G/LCO) film with a different number of layers of graphene atoms.

Another pivotal issue in studying the „graphene–metal" systems is the calculation of charge distribution. The Mulliken method traditionally used in such calculations often gives overstated and unrealistic results [10]. Within this study, charges on atoms of two-dimensional films (G/LCO) obtained using Mulliken, Hirschfield and Voronoi methods will be compared.

1. Methodology

The search for the equilibrium state of the considered objects and calculation of their electronic structure was carried out using the density functional theory (DFT) in the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof functional (PBE). All calculations were made using SIESTA 5.2.2 software [11]. For lithium (Li) and cobalt (Co) the basis set DZP was used, while for carbon (C) and oxygen (O) — DZ set. The cut-off energy for the grid in real space was set at 600 Ry. The Brillouin zone integration was carried out according to Monkhorst-Pack scheme $6 \times 6 \times 1$. Van Der Waals interaction was taken into account using Grimm correction DFT-D3.

The unit cell of a three-dimensional LCO crystal of the spatial group R=3m consisted of 12 atoms with the following sizes and angles of a periodic box: $a = b = 2.88$ Å, $c = 14.36$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$. The use of Hubbard correction for $3d$ orbitals of cobalt atoms allowed us to obtain a band gap of 2.6 eV, which corresponds to experimental data from [12,13].

The quantum capacitance for the studied structure is found using the formula:

$$\mathbf{C_q} = \frac{e^2}{m} \int_{-\infty}^{+\infty} D(E) F_T(E - \mu) dE, \tag{3}$$

where e — is a unit charge, m — is the mass of the structure, $D(E)$ — is the area under the density curve of electronic states in the considered energy range, F_T — is the thermal expansion function, μ — is the applied potential corresponding to the Fermi level shift. The surface charge σ (C/g) may be found as an integral of the differential quantum capacitance curve:

$$\sigma = \int_0^{\mu} C_q^{\text{diff}} d\mu. \tag{4}$$

According to Mulliken method, the charge on the atom q_A is found from the nucleus charge Z_A, density matrix $P_{\mu\nu}$ and matrix of S $_{\nu\mu}$ orbitals overlapping:

$$q_A = Z_A - \sum_{\mu \in A} \sum_{\nu} P_{\mu\nu} \frac{S_{\mu\nu} + S_{\nu\mu}}{2}, \tag{5}$$

where μ — index of orbital belonging to A, and ν — index of orbital of the adjacent atom. As follows from formula (5), the electron density in the region of orbital overlap is divided in half between atoms, which often leads to an overestimation of the charge localization on atoms.

The atom charge q_A as per Hirschfield is found through the electronic density of molecule $\rho(\mathbf{r})$:

$$q_A = Z_A - \int w_A(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}, \tag{6}$$

where $w_A(\mathbf{r})$ is the area of an electron, defined as the ratio of the electron density of an isolated atom A $\rho_A^0(\mathbf{r})$ to the sum of the electron densities of the remaining isolated atoms at this point $\sum_B \rho_B^0(\mathbf{r})$:

$$w_A(\mathbf{r}) = \frac{\rho_A^0(\mathbf{r})}{\sum_B \rho_B^0(\mathbf{r})}. \tag{7}$$

This element of the molecule electron density distribution is more physically justified than a simple division in half.

According to Voronoi strain density method, each atom is assigned its own disjoint region, inside which is the integral of the strain density:

$$q_A = \int \left(\rho(\mathbf{r}) - \sum_B \rho_B(\mathbf{r}) \right) d\mathbf{r}. \tag{8}$$

Thus, Voronoi approach is based on a geometry and does not depend on the choice of a basis, which significantly reduces numerical artifacts.

2. Results

At the initial stage, the translation vector of the unit cell of the three-dimensional LCO crystal, directed along the axis Z, was assumed to be $c = 200$ Å in order to exclude interlayer interaction between samples as a result of translation. Thus, a unit cell of a two-dimensional LCO film was obtained (Fig. 1, *a*). The spatial group of diatomic graphene coincides with the spatial group of LCO, which greatly simplifies modeling. However, parameters of the two-atom graphene lattice and LCO differ (2.46 and 3.08 Å respectively). To coordinate the lattice parameters, the unit cells of both structures were expanded. As a result, when the number of LCO cells turned out to be 4, and the number of graphene cells — 5, their lattice parameters became practically equivalent (12.32 and 12.30 Å accordingly). As a result of the double optimization the super-cells G/LCO of the translation vector along X and Y axes turned out to be $a = b = 12.35$ Å (Fig. 1, *b*). The mass of one LCO cell was ~ 8 the mass of one graphene layer, i.e. the mass ratio m(LCO):m(G) = 8:1. The interlayer distance between graphene and LCO turned out to be equal 2.24 Å, which correlates well with both HRTEM image data [6] and previous DFT calculations [14]. The average charge on the atoms according to Mulliken, Voronoi and Hirschfield is shown in Fig 1, *d*. As can be seen from the figure, the Mulliken charges turn out to be significantly overestimated in modulus for all atoms of the structure in comparison with Voronoi and Hirschfield. It is also noteworthy that, according to Mulliken, carbon atoms turn out to be electronegative, while according to Voronoi and Hirschfield methods, they are positive. In the end, we get a completely opposite effect of LCO-graphene interaction. According to Mulliken, graphene is the charge acceptor and takes on „colossal“ value of 3.63e, and according to Voronoi and Hirschfield, graphene loses charge (0.28e and 0.57e, respectively).

The increase in the mass fraction of carbon in G/LCO composite was carried out by increasing the number of graphene layers. Atomic supercell of a two-dimensional G/LCO layer with eight graphene layers (i.e. with the ratio of mass fractions m(LCO):m(G) = 1:1) is shown in Fig. 1, *c*. Table 1 shows the dependences of EB formation energy, Fermi level of EF, and the distance between LCO and graphene L on the mass fraction of carbon. As the mass fraction of carbon rises, the modulus binding energy decreases, which may indicate a less strong bond between graphene layers than between graphene and LCO. Another reason for this dependence may be a slight increase in the distance between LCO and the top layer of graphene. When adding a second graphene layer, a drastic shift of the Fermi level to the left is noticeable, while further addition of graphene layers shifts the Fermi level to the right, but not so noticeably.

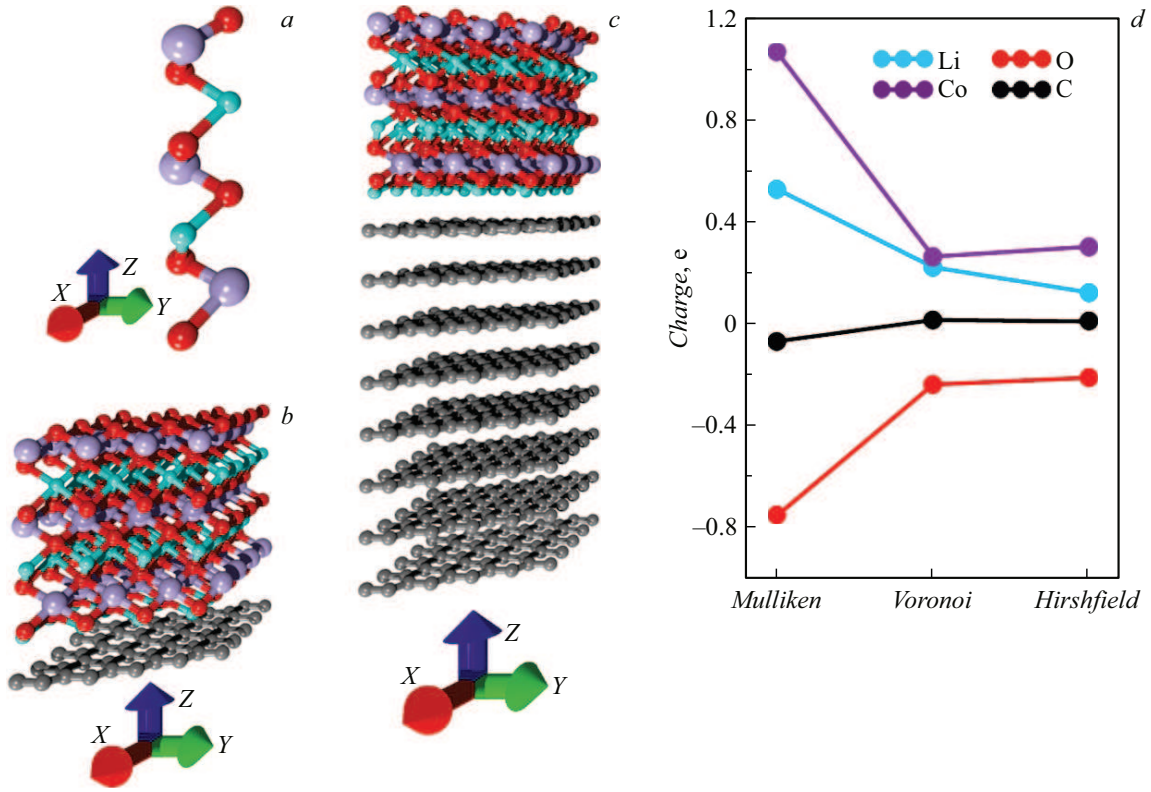

Figure 1. Atomic structures: *a* — unit cell of a 2D LCO film; *b* — supercell of a 2D G/LCO film with one layer of graphene (m(LCO):m(G) = 8:1); *c* — supercells of a 2D G/LCO film with eight layers of graphene (m(LCO):m(G) = 1:1); *d* — average charge on the atoms of a 2D G/LCO film with one graphene layer as per Mulliken, Voronoi and Hirschfield methods.

Table 1. Basic geometric and energy characteristics of a two-dimensional G/LCO film with a different mass fraction of carbon

m(LCO : m(G)	E_B, eV	E_F, eV	L, Å	$C_Q(0)$, F/g	σ_A (H_2O), C/g	σ_C (H_2O), C/g	σ_A/σ_C (H_2O)	σ_A (IL), C/g	σ_C (IL), C/g	σ_A/σ_C (IL)
8:1	−6.88	−6.82	2.24	245.0	352.8	512.3	0.69 (K)	1398.6	1973.2	0.71 (K)
4:1	−6.70	−7.28	2.31	226.1	311.4	508.8	0.61 (K)	1271.2	1911.5	0.67 (K)
2:1	−5.92	−7.22	2.33	183.6	292.3	471.6	0.62 (K)	1110.6	1766.1	0.63 (K)
1:1	−5.23	−7.15	2.36	113.0	255.0	426.6	0.60 (K)	910.3	1555.8	0.59 (K)

Table 2 shows the dependence of the charge value according to Mulliken, Hirschfield and Voronoi on the number of graphene layers. Again, attention is drawn to the complete discrepancy between Mulliken charges and more physical methods. According to Voronoi method, adding a second layer reduces the amount of charge flowing to lithium-cobalt oxide almost twice; according to Hirschfield method, adding a second layer also reduces the charge exchange, but not so significantly. A further increase in graphene layers does not affect the amount of charge transferred according to both Voronoi and Hirschfield methods.

Graphs of the quantum capacity and specific charge of a two-dimensional G/LCO film depending on the number of graphene layers are shown in Fig. 2. As can be seen from the figure, a slight increase in quantum capacitance is observed in the region 0 V with an increase in the number of graphene layers (Table 1), due to the graphene contribution to the density of electronic states near Fermi level. Yet, when closer to the electrochemical window for water (±0.6 V) the quantum capacitance of the composite with increased carbon mass fraction goes down (Fig. 2, *a*). At the same time, a sharp increase in quantum capacitance is observed in $0.5 < U < 0.6$ V segment, indicating the highest possible charge rate in this range. In the left and right edges of the working potentials for the ionic liquid (IL) (Table 1) (±1.2 V) there's even a higher trend of the quantum capacitance decline with the increase of the

Table 2. Dependence of the charge on carbon atoms on the number of graphene layers in a two-dimensional G/LCO film

Method	1	2	4	8
Mulliken	−3.62	−3.87	−3.85	−3.80
Voronoi	0.28	0.13	0.14	0.14
Hirschfield	0.57	0.44	0.44	0.44

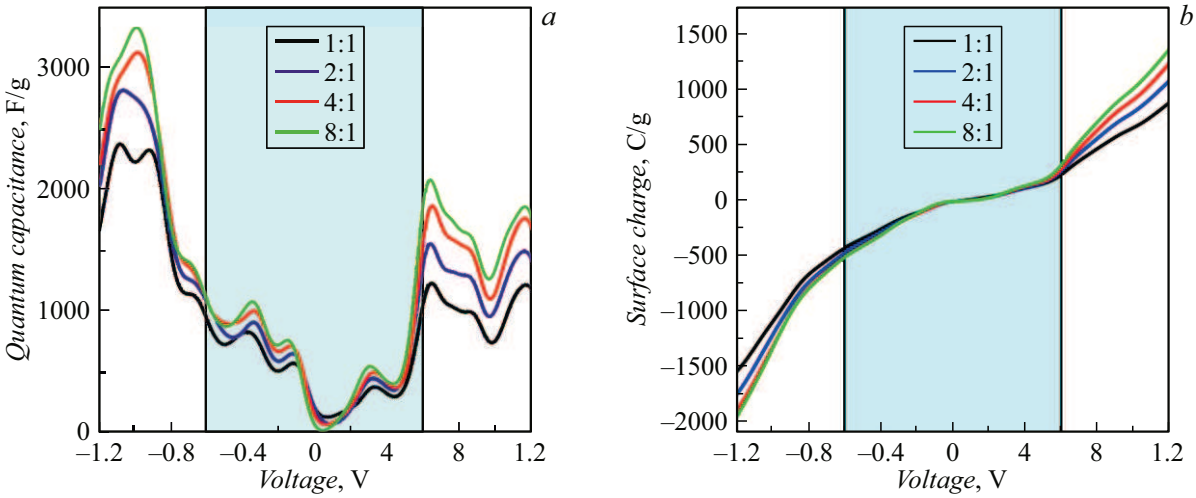

Figure 2. Quantum capacitance and specific charge of 2D films of G/LCO depending on the mass ratio of components m(G):m(LCO).

graphene layers. Based on the specific charge versus voltage curve, it can be concluded that a particular material is preferable as a cathode or anode for a chemical current source. If the charge modulus on the left edge of the electrolyte's operating range (σ_C) is noticeably larger than on the right one (σ_A), then the material is a cathode (C in Table 1), otherwise, the material is an anode. As can be seen from Table 1, the considered supercells of the two-dimensional G/LCO films exhibit pronounced cathode properties in the working windows of water and ionic liquid ($\sigma_A/\sigma_C < 0.71$), regardless of the mass ratio of the components.

Conclusion

Atomic supercells of two-dimensional G/LCO films with different mass ratios of components controlled by the number of graphene layers have been obtained for the first time within the density functional theory method. All cells were formed exothermically. The calculation of charges on atoms by various methods has shown that the charges according to Mulliken method are greatly overestimated in comparison with charges according to Voronoi and Hirschfield. Thus, it is the latter two methods that should be considered when calculating the redistribution of charges on atoms for such systems. Our calculations showed that the quantum capacitance of 2D G/LCO films increased near 0 V from 113.0 F/g in case of one graphene layer and mass concentration of m(LCO):m(G) = 8:1 up to 245.0 F/g in case of eight graphene layers and mass concentration m(LCO):m(G) = 1:1. When approaching the operating ranges of the ionic liquid ±1.2 V, the quantum capacitance decreases with an increase in the mass fraction of carbon. According to the obtained curves of the surface charge density versus voltage, all the considered composites are preferably the cathodes for supercapacitors if water or an ionic liquid act as an electrolyte.

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Conflict of interest

The authors declared that they had not any conflict of interests.

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