Investigation of the graphene–electrolyte interface in Li-air batteries: A molecular dynamics study

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Abstract. In this work the behavior of the main reactants (Li$^+$, O$_2$) of the oxygen reduction reaction (ORR) in acetonitrile solvent near the multi-layer graphene edge has been studied. It was observed by molecular dynamics simulations that the concentration distributions of the Li$^+$ and O$_2$ represent a “chessboard” structure. It was ascertained that the concentrations of the lithium ions and oxygen molecules reach their maximum values near the graphene edges pushed out from the surface, which may act as nucleation centers for the formation of crystalline products of the ORR. The maps of the free energy were estimated for the Li$^+$ and O$_2$. Energy optimal trajectories for the adsorption of oxygen molecules and lithium ions were found. Moreover, the distributions of the electric potential were obtained near the following carbon surfaces: single- and multi-layer graphene edge, graphene plane, which shows the qualitative differences in the double-layer structure.

1. Introduction

The increase of usage of the devices with high power consumption requires the development of new batteries with improved characteristics. Li-air batteries arouse particular interest among the most promising electrochemical sources due to expected very high energy density of about 1000–1500 Wh/kg that multiply exceeds that value for widely used Li-ion batteries (200 Wh/kg) [1–3]. However, the properties of the currently developed prototypes are still far from the theoretical limits. One possible solution of this problem is to develop a new cathode materials based on carbon powders, nanotubes and fibers, and graphenes [4].

A number of papers reported on the crucial role of the cathode morphology in the batteries efficiency. For example, it was shown that the mesoporous volume influences the deposition of the ORR products and, as a result, the discharge capacity [5–7]. The usage of the cathodes doped by nitrogen and sulphur allowed to accelerate the oxygen reduction reaction [8–11]. It is observed that surface geometry influences the kinetics of heterogeneous processes. Thus, the enhanced formation of Li$_2$O$_2$ at graphene edges is experimentally observed [12]. In the works [13, 14], the unique electrocatalitic properties of the graphene edge (namely rapid electron transfer and high specific capacitance) were underlined. In the work [15] cup-stacked carbon nanotubes with different amount of graphene edges on the surface were investigated. The essential difference in the ORR reaction products deposition was observed, and, in addition, nanotubes that had many reactive edges, shows higher discharge voltage and higher discharge capacity. When explaining the effect of the morphology of the cathode, one focuses on the electronic structure of the surface...
and reactants [16,17]. However, the contribution of the cathode–solvent interface structure is overlooked.

Method of molecular dynamics (MD) is widely used to explain mechanisms of various processes at the molecular level [18–21]. Thus, it was shown by MD simulation that a liquid has an ordered structure at crystal surfaces [18,21–25], and this ordering influences the kinetics of heterogeneous processes [21,23,26].

In our previous works [27,28], it was observed that surface topography strongly influences the cathode–solvent interface structure. We have already calculated the concentration distributions of the main reactants of the oxygen reduction reaction (Li$^+$, O$_2$) near the edge and plane of a single-layer graphene [27]. However, an open question also remains about distributions and adsorption kinetics of the ORR reactants near the multi-layer graphene edge. This surface is especially interesting because of the qualitatively different chessboard interface structure [27,28]. Also, in this work the distribution of the electric potentials is calculated as one of the key factors influences the polar and charged particles distributions in the double-layer.

2. Computational details

We used an orthorhombic simulation box to investigate the behavior of the reactants of the oxygen reduction reaction. It contains acetonitrile (ACN) layer confined on both sides by surfaces of the perpendicularly oriented to the interface multi-layer graphene with an area of 4.3 × 4 nm$^2$ each. The width of the solvent layer was about 4 nm, to avoid interference between surfaces. The system contained 733 ACN molecules to ensure 1 bar pressure in the liquid phase. The all-atom model developed by Nikitin et al was used for ACN molecules [29]. We chose armchair graphene edge for study. Hydrogen atoms were attached to the graphene edges. In order to calculate van der Waals interactions AMBER force field was used [30]. Carbon atoms in the graphenes were fixed during the simulation, while hydrogen atoms attached to the graphene edges were flexible. C–H bond parameters and atomic charges were equal to those of the benzene [31], that satisfactorily agrees with the DFT calculations [32]. The MD simulation was performed in the NVT ensemble at temperature $T = 300$ K kept constant using Nose–Hoover thermostat. The Ewald method with a real space cutoff value of 1 nm was used to calculate the electrostatic interaction. The equations of motion were solved using the Verlet leapfrog integration algorithm with a time step of 1 fs. The van der Waals cutoff radius was 1 nm. 3D periodic boundary conditions were used. Periodicity in the direction normal to the surfaces was increased to 22 nm to reduce the interactions with the periodic images.

In order to obtain the Li$^+$ and O$_2$ concentration distributions a series of MD simulations were run where the particle was fixed with the harmonic potential at a given distance from the surface remaining unrestrained in parallel to the surface. From the data collected during 1 ns, the distributions of the ORR reactants were calculated for a predetermined distance from the surface, taking into account their periodicity and symmetry. The distance from the surface was varied with the step of 0.5 Å.

We used the potential of mean force (PMF) along the direction oriented perpendicularly to the cathode surface to combine the distributions obtained for different distances into 2D concentration distribution map. The PMF was computed in a manner described in our previous work [27] with the averaging time for every point of 1 ns and integration step of 0.5 Å. PMFs were converted to the concentration using the Boltzmann equation: $C(x) = C_0 \exp(-U(x)/kT)$, where $U(x)$ is the PMF.

To study the electric-potential distribution depending on the carbon surface morphology, we used simulation box which contained 3 types of the surfaces. It was described in our work [27]. 3D Ewald method with the corrections proposed in work [33] was used, in view of the slab geometry of the simulation box. Averaging time was 5 ns. For obtaining the electric potential distribution 2D Poisson’s equation was solved by the Successive Over Relaxation (SOR) method
on a regular square grid with steps of 0.2 Å. We used periodical boundary conditions along the y direction and zero Neumann boundary condition along the x direction [27, figure 1].

We used the DL_POLY classic package to perform MD simulations [34]. The calculations were run on the supercomputers MVS-100K and MVS-10P (Joint Supercomputer Center of the Russian Academy of Sciences), “Lomonosov” (Moscow State University) [35] and Supercomputer Centre of JIHT RAS.

3. Results and discussion
3.1. Distributions of the oxygen reduction reaction reactants
Maps of the equilibrium concentration distributions of the ORR reactants O$_2$ and Li$^+$ near the multi-layer graphene edge are shown in figure 1. Distributions are normalized to the bulk concentration $C_0$.

We have equilibrium distributions if rate of the electrochemical processes is significantly less than the rate of adsorption of the reactants. It can be seen that oxygen molecules and lithium ions are mostly located in the density maxima of the solvent [27, figure 1]. The highest local concentration of the oxygen is observed opposite the graphene edges pushed out from the surface (in contrast to solvent for which the highest density peak was opposite the deeper edges) and exceeds the average bulk concentration 3.2 times. The concentration peaks of lithium ions near the deeper edged are not found due to the electrostatic repulsion from positively charged hydrogen atoms on the graphene edges. Maximum local concentration of the Li$^+$ is more than 5 times larger than the average bulk one. From the fact that the maximum concentration of the reactants is observed opposite the graphene edges pushed out from the surface, one can suppose that these edges act as nucleation and growth centers of the ORR crystalline products.

3.2. Adsorption free energy profile of the reactants at the surface
For thermodynamic analysis of the ORR reactant adsorption, the free energy profiles were determined from concentration distributions using the Boltzmann equation. The free energy profiles for O$_2$ and Li$^+$ are shown in figure 2. It can be seen that maxima of the free energy are located in “chessboard” order. This allows particles to be adsorbed avoiding high-energy states. The possible lowest energy pathways are schematically depicted in figure 2 by red lines. It is
Figure 2. Free energy profiles for $\text{O}_2$ (a) and $\text{Li}^+$ (b). Red lines schematically show the lowest energy adsorption pathways.

Figure 3. Electric potential distributions near (a) the multi-layer graphene plane, (b) the single-layer graphene edge, and (c) the multi-layer graphene edge.

also be noted that the adsorbed oxygen molecules (the closest to the surface free energy local minima) can diffuse along the cathode surface without any significant potential barriers.

3.3. The electric potential distributions
We show the electric potential distributions near the three following cathodes: multi-layer graphene plane, graphene nanoribbon and multi-layer graphene edge in figure 3. The region of the electric field inhomogeneity is seen near all the surfaces. It extends over $\sim$15 Å. This value corresponds to the spatial correlation length in acetonitrile. Near the plane of the single- and multi-layer graphene the layered structure is observed. The period of the layered structure is about 4 Å, that corresponds to the size of ACN molecules. Near the edge of single-layer graphene the layered structure is also observed but the layers have curvature due to the curved nature of the surface. Near the edge of multi-layer graphene it can be seen the chessboard order of the peaks and valleys of the electric potential. One can also find the potential drop...
of about 3 V at the multi-layer graphene edge associated with polar C–H bounds located on
the graphene edges. At the other surfaces there are no significant potential jumps. The electric
potential distribution affects the behavior of polar and charged particles at the double layer
and particularly explains the differences between distributions of lithium cations and oxygen
molecules near the multi-layer graphene edge depicted in figure 1.

4. Conclusion
MD simulations were used to study the distribution of the main reactants of the oxygen reduction
reaction near the multi-layer graphene edge. From calculated distributions it follows that
lithium ions are adsorbed only on the pushed out from the surface graphene edges. In this area
concentration of the oxygen molecules is the highest too. This suggests that pushed out graphene
edges may act as nucleation centers for the formation of crystalline discharge products. The free
energy profiles were also obtained for O$_2$ and Li$^+$ near the multi-layer graphene edge, from
which we found the lowest energy adsorption pathways. Along these pathways particles can be
adsorbed avoiding high energy states. Also, it is observed that adsorbed oxygen can diffuse along
the cathode surface without any significant barriers. Moreover, we compute the distributions of
the electric potential near the studied cathodes, which show that cathode topography variations
arouse qualitative changes in the double-layer structure.

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