Supporting Information for:

"First-Principles Study of Adsorption-Desorption Kinetics of Aqueous V^{2+}/V^{3+} Redox Species on Graphite in a Vanadium Redox Flow Battery"

Zhen Jiang,[a] Konstantin Klyukin,[a] and Vitaly Alexandrov*[a,b]

I. Static DFT calculations

To study (0001), $(11\bar{2}0)$ and $(10\bar{1}0)$ graphite surfaces we employed periodic slab models comprised of two, five and six atomic layers with a vacuum gap of 15 Å, while surface dimensions were 9.78 × 9.78 (4 × 4 unit cell), 13.54 × 8.47 (2 × 2 unit cell) and 13.54 × 7.34 Å^2 (2 × 3 unit cell), respectively. Monkhorst-Pack k-points grids of 2 × 2 × 1, 3 × 2 × 1, and 3 × 2 × 1 were used for the (0001), $(11\bar{2}0)$, and (1010) surfaces, respectively. Surface energies E_{surf} were computed as

$$E_{surf} = (E_{slab} - n \times E_{bulk}) / (2 \times A_{surf})$$

where E_{slab} is the total energy of the slab, n is the number of bulk units, E_{bulk} is the total energy of the bulk, and A_{surf} is the surface area. For optimization of graphite (0001), carbon atoms in both layers were allowed to relax, while the middle layers of graphite (1120) and graphite (1010) were fixed during optimization.

II. Car-Parrinello molecular dynamics simulations

Car-Parrinello molecular dynamics (CPMD) simulations were carried out using the the Perdew-Burke-Ernzerhof (PBE) functional corrected for van der Waals interactions using the Grimme approach (PBE-D4) with the kinetics cutoff energies of 100 and 200 Ry were applied to expand the Kohn-Sham electronic wave functions and charge density, respectively. The aqueous systems were initially pre-equilibrated using a QM/MM potential during 20 ps followed by additional CPMD equilibration for ~5 ps. Hydrogen atoms were replaced with deuterium to facilitate numerical integration. A fictitious electronic mass of 600 au and a simulation time step of δt = 5 au (0.121 fs) were set. Configurations from the post-equilibration CPMD simulations used for further analysis were saved at time intervals of 10δt.

CPMD-based metadynamics technique was employed to compute the free energy profiles of adsorption and desorption reaction at 300 K for

[a] Prof. Dr. V. Alexandrov
Department of Chemical and Biomolecular Engineering
Nebraska Center for Materials and Nanoscience
University of Nebraska-Lincoln
1400 R Street, Lincoln, Nebraska 68588, USA
E-mail: valexandrov2@unl.edu
[b] Z. Jiang, Dr. K. Klyukin
Department of Chemical and Biomolecular Engineering
University of Nebraska-Lincoln
1400 R Street, Lincoln, Nebraska 68588, USA

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aqueous V^{2+} and V^{3+} cations to estimate free-energy barriers adsorption/desorption. The bond distance between a vanadium ion and an O atom on the surface was used as the collective variable (CV) to describe the adsorption and desorption processes. Metadynamics simulations at 300 K were performed using equilibrated geometries picked from the last block of the CPMD production runs. The height of the repulsive Gaussian hills was set to 0.0005 a.u. (0.315 kcal/mol) and 0.001 a.u. (0.630 kcal/mol) for V^{2+} and V^{3+}, respectively, and the width was 0.0707 a.u. Gaussian hills were added to the potential every 100δt for both two vanadium ions.

Figure S1 shows the change of the CV (the distance between adsorbing V ion and surface O atom) as a function of the number of Gaussian functions used to reconstruct the free energy profile. For V^{2+}, the distance equal to 3.898 Å represents the most stable configuration of the outer-sphere structures on the hydroxlated graphite surface, while 2.188 Å is the distance for the inner-sphere adsorption configuration. In the case of V^{3+}, 1.989 Å indicates the inner-sphere adsobed structure and 4.057 Å is the distance for the outer-sphere V^{3+} complex. The partial snapshots for the V ions‘ desorption and adsorption reactions can be found in the Figure 2 (a) in the article. It is seen that the added numbers of Gaussians, forcing vanadium ions to fall into the energy valley of the product state, were 830, 960, 680, and 430 in Figure S1 (a), (b), (c), (d), respectively. The corresponding numbers of Gaussian hills were chosen to reconstruct the free energy profiles for the adsorption and desorption reactions of V^{2+} and V^{3+} (see Figure 2 (c) in the article). Also, Figure S2 demonstrates a very small dependence of the free-energy barrier for adsorption/desorption of V^{2+} species as a function of the Gaussian hill height (0.0005 a.u. versus 0.001 a.u.).

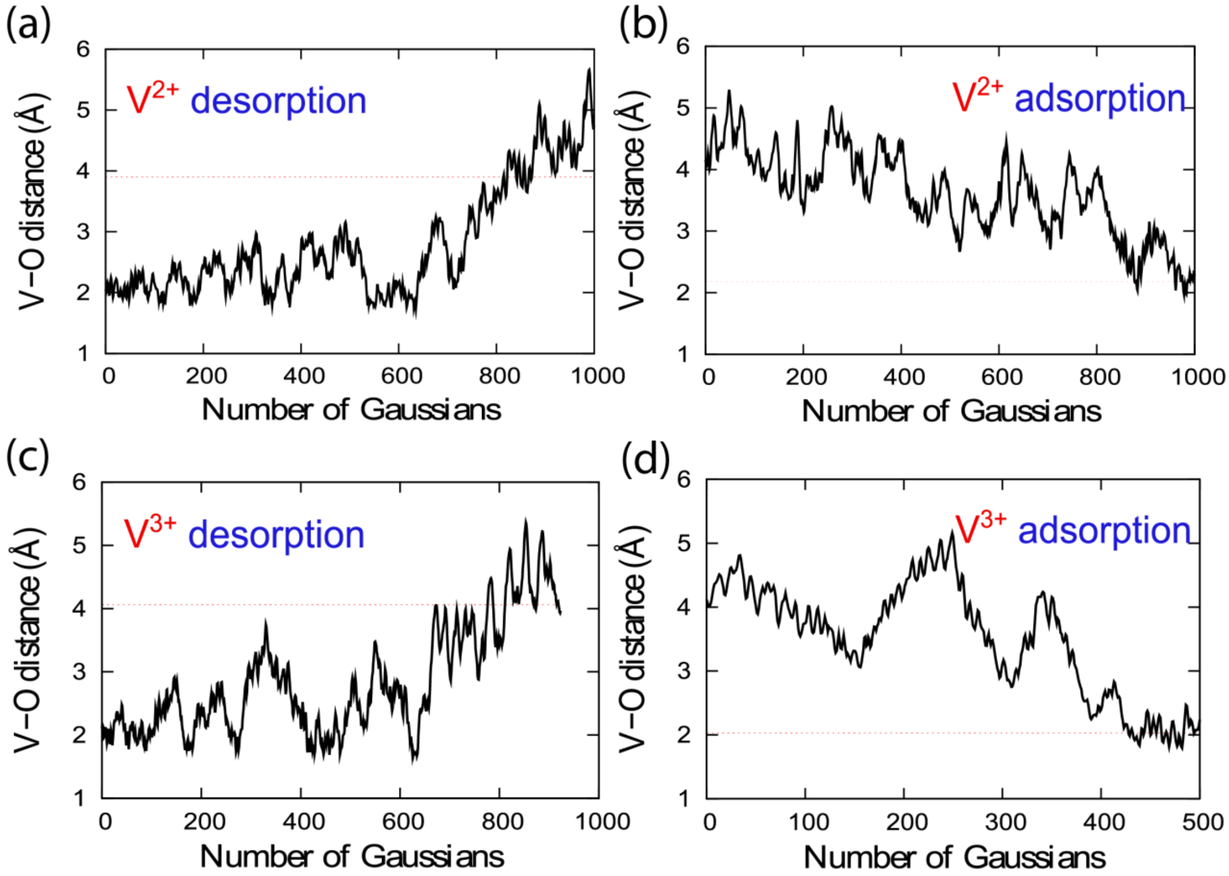

Figure S1. Evolution of the collective variable (the distance between V ions and surface O atom) with respect to the number of Gaussian functions during the process of adsorption and desorption of aqueous V^{2+} and V^{3+}.

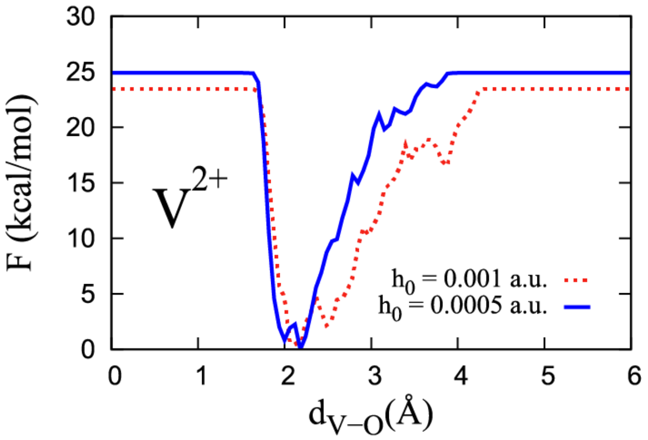

Figure S2. Activation barriers of desorption reaction of aqueous V^{2+} employing two different Gaussian heights (h_0) in CPMD metadynamics simulations.