

How NiOOH electrode in Ni-MH battery works:
First principles molecular dynamics analysis

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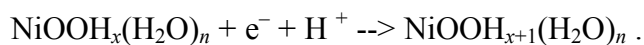
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Ni-MH secondary battery has been used widely for a long time in electronic devices and hybrid cars. In the present Ni-MH battery, nickel hydroxide (NiOOH) is completely used with a valance change between Ni(II) and Ni(III). Even though more than a single electron transfer, 1.5 electron, is possible, a problem is less cycling performance. Some additional atoms or ions to the NiOOH electrode can improve the performance. Its mechanism is not known, however. In order to understand how NiOOH electrode works from an atomistic point of view, we performed the first principles molecular dynamics (FPMD) simulations.

Electronic structure calculations in the FPMD are based on DFT with ultrasoft-pseudopotentials for the inner core electrons and PBE functional for the exchange correlation. Program code "STATE" is used. MD is at a constant temperature 353 K by a simple-velocity-scaling thermostat.

Three crystal structures, α , β , and γ , are known for NiOOH in the layer structure with the different stacking sequentials. It is more correctly written as NiOOH_x in a mixed valence of Ni(4-x) with H₂O and some ions between layers. Structure β is a general form in the secondary batteries of one electron transfer. If more than one electron charging/discharging is applied to the β -NiOOH_x electrode, structure change may occur, resulting in a low cycling performance.

Electron transfer reaction is generally written as



Energy difference for compositions of $x+1$ and x gives the electric power, EMF, against RHE as

$$\text{EMF} = d[\text{E}(\text{NiOOH}_x(\text{H}_2\text{O})_n) - x\text{E}(\text{H}_2)/2]/dx$$

We have calculated EMF from time averaged total energy with different number of H atoms. A typical system contains 12 formula units of NiOOH_x in a FPMD unit cell. In the case of α -structure, 36 units are in three times larger cell in the c -direction. Two snapshots of FPMD trajectories are shown, for examples, in Figure. Ni layer becomes very distorted and H₂O molecules are moving with proton jumps.

Calculation for various systems showed that EMFs change smoothly as a function of number of H. They are in the reasonable values of 1.0~1.5 V vs. RHE except at Ni valences near 2 or 4. There is a small EMF jump at Ni valence 3. Systems we have calculated are α , β , and γ -NiOOH_x with and without additional atoms, Ga or Al.

From the calculations, it looks easy to attain 1.5 electron transfer in NiOOH_x electrode. But, no phase transition is included in the calculations. In the layered systems, a large volume change is possible with a small change of the total energy, particularly in the c -direction. Cell deformations are also possible. These features may relate to the structure change by charging/discharging of more than one electron.

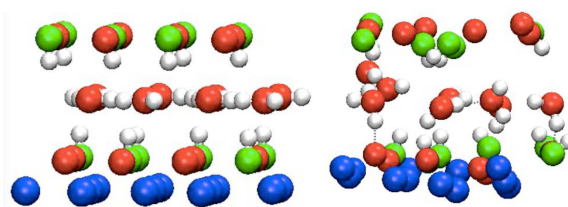


Fig. Initial (left) and final (right) structures in FPMD simulations of NiOOH_x electrode, β - $(\text{Ni}_{12}\text{O}_{24}\text{H}_n(\text{H}_2\text{O})_8)$.