Supplementary Information: Charge Density and Redox Potential of LiNiO₂ Using Ab Initio Diffusion Quantum Monte Carlo

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Overview of Diffusion Monte Carlo Method

DMC estimates the ground state energy of the many-body wave function by simulating the Schrödinger equation in imaginary time, $\tau = it$:

$$\frac{\partial}{\partial \tau} \Psi(R, \tau) = (-\frac{1}{2} \nabla^2 + V - E) \Psi(R, \tau)$$ (1)

where $V$ and $\nabla^2$ are the potential and kinetic energy operators, $\Psi(R, t)$ is the wavefunction and $E$ is the ground state energy offset in equation 1. Electrons are propagated in imaginary time until a steady state is reached with a desired statistical error bar on the ground state energy. At the steady state, populations of high energy electronic configurations have decayed and the exact ground state for the given nodal surface is projected out. We use fixed-node DMC (FN-DMC) where the nodal surface of the trial wavefunction is fixed during the simulation, in order to avoid the Fermion sign problem. DMC total energies are variational with respect to the quality of the nodal surface: with the exact nodal surface, DMC can arrive at the exact ground state energy.\(^1\)

For most solid state calculations, the trial wave function is typically obtained from DFT calculations. Single particle DFT orbitals are then parametrized using Jastrow factors to construct the many-body trial wave function:

$$\Psi(R, \tau) = D^\uparrow(R)D^\downarrow(R)e^{-(J_1 + J_2 + J_3)}$$ (2)

where $D^\uparrow$ and $D^\downarrow$ are the spin up and spin down Slater Determinants obtained from DFT calculations. $J_1$, $J_2$ and $J_3$ terms are the one-body, two-body and three-body Jastrow terms respectively. One body terms represent the electron-ion interactions, two body terms represent the electron-electron interactions and three-body terms represent electron-electron-ion interactions. Jastrow parameters are usually optimized using variational Monte Carlo (VMC) calculations which typically recover 60-90% of the total valence correlation energy.\(^2\)
Structural parameters and magnetic moments of Li$_x$NiO$_2$ structures

Table S1: Lattice parameters and the total magnetic moments for the 4 formula unit cells of Li$_x$NiO$_2$ structures optimized using PBE

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (deg)</th>
<th>β (deg)</th>
<th>γ (deg)</th>
<th>Volume (Å$^3$)</th>
<th>μ (μ$_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO$_2$</td>
<td>5.59</td>
<td>5.59</td>
<td>4.98</td>
<td>73.71</td>
<td>73.71</td>
<td>60.00</td>
<td>127.73</td>
<td>0</td>
</tr>
<tr>
<td>Li$_{0.25}$NiO$_2$</td>
<td>5.58</td>
<td>5.65</td>
<td>5.88</td>
<td>62.35</td>
<td>61.64</td>
<td>60.36</td>
<td>135.57</td>
<td>1</td>
</tr>
<tr>
<td>Li$_{0.5}$NiO$_2$</td>
<td>5.74</td>
<td>5.74</td>
<td>5.10</td>
<td>58.75</td>
<td>73.91</td>
<td>73.91</td>
<td>136.24</td>
<td>2</td>
</tr>
<tr>
<td>Li$_{0.75}$NiO$_2$</td>
<td>5.76</td>
<td>5.76</td>
<td>5.83</td>
<td>60.42</td>
<td>60.42</td>
<td>60.00</td>
<td>137.96</td>
<td>3</td>
</tr>
<tr>
<td>LiNiO$_2$</td>
<td>5.02</td>
<td>5.02</td>
<td>5.77</td>
<td>90.08</td>
<td>89.92</td>
<td>70.82</td>
<td>136.81</td>
<td>4</td>
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</tbody>
</table>

Li intercalation voltages

Table S2: Li intercalation voltages (in V) from DFT and DMC. Data presented here is plotted in Figure 2 in the main text.

<table>
<thead>
<tr>
<th></th>
<th>PBE</th>
<th>PBE+U=3</th>
<th>PBE+U=6</th>
<th>PBE+U=9</th>
<th>DMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO$<em>2$ - Li$</em>{0.25}$NiO$_2$</td>
<td>3.81</td>
<td>4.21</td>
<td>4.73</td>
<td>5.06</td>
<td>4.61 ± 0.14</td>
</tr>
<tr>
<td>Li$_{0.25}$NiO$<em>2$ - Li$</em>{0.5}$NiO$_2$</td>
<td>3.35</td>
<td>3.77</td>
<td>3.32</td>
<td>4.72</td>
<td>4.40 ± 0.02</td>
</tr>
<tr>
<td>Li$_{0.5}$NiO$<em>2$ - Li$</em>{0.75}$NiO$_2$</td>
<td>3.12</td>
<td>3.52</td>
<td>4.02</td>
<td>4.46</td>
<td>3.91 ± 0.02</td>
</tr>
<tr>
<td>Li$_{0.75}$NiO$_2$ - LiNiO$_2$</td>
<td>2.90</td>
<td>3.11</td>
<td>3.83</td>
<td>4.46</td>
<td>3.61 ± 0.20</td>
</tr>
</tbody>
</table>
Finite size extrapolations

Figure S1: DMC finite size extrapolations for the calculated Li_xNiO_2 cells: a) NiO_2, b) Li_{0.25}NiO_2, c) Li_{0.5}NiO_2, d) Li_{0.75}NiO_2 and e) LiNiO_2. Ewald and MPC are the different methods to calculate the conditionally convergent 1/r interaction, where MPC stands for Model Periodic Coulomb.
Charge Density Distributions

Figure S2: a) Radial total density ($\rho = \rho_\uparrow + \rho_\downarrow$) and b) radial total density differences from extrapolated DMC density ($\rho^{DMC-ext}$) around the Ni atom.
Figure S3: a) Radial spin density and b) radial spin density difference from extrapolated DMC around the O atom with various theoretical methods using RRKJ pseudopotentials.
Density of States

Figure S4: Density of states for LiNiO$_2$ using a) PBE, b) PBE+$U=3$, c) PBE+$U=6$, d) PBE+$U=9$, e) SCAN functionals. Densities are projected on Ni-$t_{2g}$, Ni-$e_g$ and O-$p$ orbitals. Vertical black dashed lines indicate the majority spin Fermi level, whereas the red dashed line shows the minority spin Fermi level.
Li diffusion barrier dependence on DFT geometries

Figure S5: Geometry dependence of Li diffusion barrier on DFT geometries, calculated for Li$_{0.5}$NiO$_2$. Saddle points are optimized using PBE and PBE+$U$=6 eV, then PBE+$U$ single point calculations are performed using these geometries. The PBE optimized saddle point yields a much larger deviation between the single point calculations, and overall the barrier energies are larger than the PBE+$U$ optimized saddle point which shows a clear monotonous trend. The PBE barrier energy at the PBE optimized saddle point is nearly 50 meV smaller than the saddle point optimized using PBE+$U$=6 eV.

Li diffusion barrier with DMC

Figure S6: DMC finite size extrapolation for the diffusion barrier calculation given in Fig. 6 of the main document for Li$_{0.5}$NiO$_2$
References

(1) Ceperley, D. M.; Alder, B. J. Ground state of the electron gas by a stochastic model. 

(2) Drummond, N. D.; Towler, M. D.; Needs, R. J. Jastrow correlation factor for atoms, 