Supporting information for:

First-principles assessment of hole transport in pure and Li-doped NiO

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S1 – Cluster construction in pure NiO

We constructed the $[Ni_2O_{10}]^{15-}$, $[Ni_{10}O_{28}]^{35-}$ and $[Ni_{28}O_{60}]^{63-}$ clusters (Figure 1 of the Main Text) used to generate diabatic Marcus curves by progressively increasing the number of ions surrounding the donor and acceptor O ions. Furthermore, we made sure that each Ni ion was coordinated octahedrally with six O ions to account for the proper crystal-field splitting between Ni $3d$ (e_g) and Ni $3d$ (t_{2g}) orbitals. We chose $a = 4.199\,\text{Å}$ as the lattice constant used to build our clusters and the surrounding APC array. This value is the equilibrium lattice constant resulting from periodic density functional theory (DFT) +U ($U - J$ = 3.8 eV) computations[1] and is in good agreement with the experimental value of $4.180\,\text{Å}$.[2]

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S2 Embedding scheme

Before we replaced the central ions by the cluster and the capping effecting core potentials (ECPs), the aperiodic point charge (APC) array contained 8000 point charges, corresponding to a 10x10x10 array of eight-atom NiO cubic unit cells. Test calculations showed that increasing the size of the array to 11x11x11 changed the calculated $\Delta G^*_{\mathrm{diab}}$ by less than 0.01 eV. Point charges with -2e and +2e charges in the APC represented the O^{2-} and Ni^{2+} ions, respectively.

S3 Achieving proper hole localization and basis sets

We ensured that the hole was localized on the relevant donor or acceptor sites by doing the following. First, we manually distorted the surrounding geometry (expanding the bonds near the hole) to make the site more electrostatically favorable for hosting the hole. Thereafter, we constructed our initial wavefunction guess for the unrestricted Hartree-Fock (UHF) calculations using the orbitals of isolated ions. In this way, we could position a hole on a specific site by changing the charge of the isolated ion used to create the initial guess corresponding to that site. We made sure that the hole was localized on the relevant site by evaluating the difference between spin up and spin down Mulliken populations for each site (*e.g.*, a difference of 0 for an O ion would indicate a closed shell O^{2-} ion, while a difference of -1 would indicate an O^{1-} ion with an O 2p orbital singly occupied by a spin down electron). We also used the initial wavefunction guess technique above to (a) make sure that the Ni^{2+} ions are anti-

ferromagnetically coupled in the [111] direction, consistent with experimental findings,[3,4] and (b) to achieve the three possible spin configurations depicted in Figure 1's inset.

We used the all-electron 6-31++G** basis set (contracted as ($11s5p1d/4s3p1d$)) for O,[5] and the Hay-Wadt VDZ basis set (contracted as ($8s5p5d/3s3p2d$)) for Ni,[6] coupled with the Hay−Wadt small core ECP that represents the Ni nucleus and its $1s$, $2s$, and $2p$ core electrons.[6] Tests showed that using the small core Stuttgart ECP and its larger corresponding basis set[7] for Ni (contracted as ($8s7p6d1f/5s5p3d1f$)) changed $\Delta G_{\mathrm{diab}}^{*}$ by less than 0.05 eV.

S4 Geometry optimization

While optimizing the geometry, we kept the capping ECPs and the APC array fixed. We further froze the O ions directly adjacent to the capping ECPs (*i.e.,* the O ions at the edge of the clusters) for $[Ni_{10}O_{28}]^{35-}$ and $[Ni_{28}O_{60}]^{63-}$, since the difference in charges on the neighboring Ni and Mg cations could lead to an unphysical distortion of the position of these O ions. We do not freeze the edge O ions in $[Ni_2O_{10}]^{15-}$ since O(A) and O (D) are edge ions.

We stopped optimizing the geometry when the maximum force component on each ion fell below 0.005 eV/Å and the root mean square force of all the force components fell below 0.002 eV/Å. This led to a total energy convergence within 0.01 meV, far below error margins that can be expected in UHF calculations. The stringent convergence conditions we used and our monitoring of the Mulliken spin populations to

ensure the desired hole localization means the results of our geometry relaxation reliably correspond to physical polarons.

S5 Cluster Choice and CASSCF calculations – pure NiO

Although we found $[Ni_{10}O_{28}]^{35-}$ to be a reasonable cluster for evaluating the diabatic Marcus curves of pure and doped NiO, we were not able to use this cluster for determining V_{AB}. The large number of singly occupied Ni $3d$ (e_g) orbitals in the $[Ni_{10}O_{28}]^{35-}$ cluster causes the active space to be prohibitively large, leading to very high computational costs for performing CASSCF calculations. We therefore estimated V_{AB} by performing CASSCF calculations on $[Ni_2O_{10}]^{15-}$ clusters.

The geometries of the carved out $[Ni_2O_{10}]^{15-}$ clusters resembled the undistorted cluster depicted in Figure 1 (a). We made sure that the relevant ions, *i.e.*, O(*A*), O(*D*), Ni (1), and Ni (2), were all included in the smaller cluster. Our decision to evaluate the adiabatic energy levels with $[Ni_2O_{10}]^{15-}$ is justified because we previously showed that using this cluster at the undistorted DFT+U geometry to study the energies associated with hole states in NiO leads to excellent agreement with measured photoemission/inverse photoemission spectra.[8]

We used two criteria to identify the relevant low-lying adiabatic states. First, each pair of adiabatic states must be (anti-)symmetrically distributed between the donor and acceptor ions, since our calculations are performed at the intermediate geometry q_C. Second, each pair must have opposite parities with respect to each other, given that the

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lower-lying and higher-lying adiabatic states are formed from the symmetric and anti-symmetric mixing of the diabatic states, respectively. We imposed C_{2v} symmetry to ensure the (anti-)symmetric distribution and to facilitate the evaluation of the parities. We chose the principal axis for this symmetry to go through the Ni-Ni axis. This ensures that the Ni ions are treated as distinct from each other, *i.e.*, they are not equivalent by symmetry. This is necessary for considering the anti-ferromagnetic case, where the two Ni ions have opposite spins.

The same embedding scheme and basis sets as in the UHF calculations were used in the CASSCF calculations. Symmetry-imposed UHF calculations on the carved-out $[Ni_2O_{10}]^{15-}$ clusters provided the initial guess for the CASSCF wavefunction. We constructed the active space by including all singly occupied orbitals, all doubly occupied orbitals with occupation number <0.98, and all virtual orbitals with occupation number >0.02. Similar to the cases we have studied previously,[8] this convergence criterion leads to an active space with 11 electrons in 12 orbitals; three (nearly) occupied O $2p$ orbitals, one singly occupied O $2p$ orbital, four singly occupied Ni $3d$ (e_g) orbitals, and four (nearly) unoccupied O $2p$ orbitals, which act as correlating orbitals for the occupied O $2p$ orbitals.

S6 Cluster Choice with Li doping

We used 38-atom clusters, similar to $[Ni_{10}O_{28}]^{35-}$, to generate the diabatic Marcus curves for the Li-doped cases, since we were successful in achieving convergence to within 0.1 eV for $\Delta G_{\mathrm{diab}}^*$ with the $[Ni_{10}O_{28}]^{35-}$ cluster in the pure NiO case (for more details

on our cluster choice, see the "Diabatic Energy Barrier – Pure NiO" section in *Results* in the Main Text). We considered cases with one and two Li ions replacing various Ni ions in the cluster (Figure 3). We did not add a hole (*i.e.*, remove an electron) for the cases with a single Li ion substitution, since the monovalency of the Li ion introduces the hole to the cluster by itself. Therefore, the clusters with a single Li in our calculations have the configuration $[LiNi_9O_{28}]^{36-}$. For cases with two Li ions, two holes are introduced by adding dopants to the cluster; however, we added an additional electron to ensure that we are able to study the transport characteristics associated with one single hole in the crystal structure. Therefore, the cases with two Li ions in our calculations are represented as $[Li_2Ni_8O_{28}]^{37-}$. These clusters were embedded in the same ECPs and APC array, and Marcus curves were generated using the same method as the undoped case. We also used identical basis sets as the undoped case for O and Ni ions as well as the all-electron 6-31++G** basis set for Li (contracted as ($11s5p1d/4s3p1d$)).[9]

S7 Models of Homogeneous Li doping

To achieve homogeneity while building the 64-atom cubic unit cell from which the 38-atom cluster models were carved out, we placed the Li ions at the corners and the centers of the cube faces. This unit cell was later used as the lattice structure on which kinetic Monte Carlo (KMC) calculations were performed (see section S8 for more information). The carved-out 38-atom clusters are used for generating the diabatic Marcus curves and represent the different hole transfer pathways associated with hole movement through the lattice formed by the 64-atom unit cell. For each cluster,

consistent with measurements,[10,11] we chose the spin of the unpaired electron on O(D) such that it was aligned with the ferromagnetic layer containing the Li ion that has introduced the corresponding hole. For more information about the carved-out 38-atom clusters, see section *Li-Doped NiO and Homogeneous Li$_{0.125}$Ni$_{0.875}$O* in the Computational Methods of the Main Text.

After generating the diabatic Marcus curves using the 38-atom clusters, consistent with the pure case, we performed CASSCF calculations on smaller clusters for evaluating V_{AB} associated with each pathway. We constructed the clusters for CASSCF calculations by carving out 12-atom clusters (similar to Figure 1 (a)) from the intermediate geometry q_C of the 38-atom Li-doped clusters that we previously carved out of the 64-atom unit cell, which represents the homogeneous Li$_{0.125}$Ni$_{0.875}$O lattice (see Computational Methods in the Main Text for more information). The converged active space for $[\text{LiNiO}_{10}]_a^{16-}$ and $[\text{LiNiO}_{10}]_b^{16-}$, corresponding to the respective $[\text{LiNi}_9\text{O}_{28}]_a^{36-}$ and $[\text{LiNi}_9\text{O}_{28}]_b^{36-}$ clusters, had 9 electrons in 10 orbitals; three (nearly) occupied O 2p orbitals, one singly occupied O 2p orbital, two singly occupied Ni 3d (e_g) orbitals, and four (nearly) unoccupied O 2p orbitals that act as correlating orbitals for the occupied O 2p orbitals.

S8 Kinetic Monte Carlo simulations

We performed KMC calculations for a hole propagating through the crystal structure formed by replicating the 64-atom unit cell (described in section S7) to simulate hole transfer through a homogenous Li$_{0.125}$Ni$_{0.875}$O sample. (The barriers

associated with hole transfer through different pathways in this crystal structure were provided using the cluster calculations explained in section S7 and section *Li-Doped NiO and Homogeneous $Li_{0.125}Ni_{0.875}O$* in the Computational Methods of the Main Text.)We started our simulation by selecting an O site next to a Li ion as our initial O(*D*). We characterized the hole transfer by (a) the time t_{ht} it takes for the hole to make the transition and (b) the acceptor site O(*A*). We determined t_{ht} for the transfer using the expression[12]

$$t_{ht} = -\frac{\ln r}{\Gamma},$$
(S1)

where *r* is a random number between 0 and 1, and Γ is the sum of all k_{ht} values associated with all the O sites available for hole transfer from O(*D*). This expression implies that for larger k_{ht} values, the time it takes for a hole to hop to an adjacent O ion is shorter. We determined O(*A*) by randomly choosing one of the neighboring O sites such that the probability of selecting each site is inversely proportional to the corresponding k_{ht} value for hopping from O(*D*) to O(*A*). After moving the time forward by t_{ht}, we restarted the process for subsequent hops by setting the previous O(*A*) as the new O(*D*).

Using the resulting polaron trajectory and an elapsed time $t = 10^{-8}$ seconds, which corresponds to ~100,000 polaron hops, we determined the mobility from[12]

$$\mu = \frac{e}{k_B T} \frac{1}{6t} < |r_i(t) - r_i(0)|^2 >,$$
(S2)

where $r_i(t)$ is the position of the polaron at time *t* in the *i* th trial run. This expression is equivalent to Eq. 1 in the Main Text for cases where hopping is explicitly simulated. We

performed 2000 trials. Increasing t and the number of trials by an order of magnitude did not change the resulting value for μ.

References

(1)   Alidoust, N.; Toroker, M. C.; Keith, J. A.; Carter, E. A. *ChemSusChem* **2014**, *7*, 195–201.

(2)   Fiévet, F.; Germi, P.; de Bergevin, F.; Figlarz, M. *J. Appl. Crystallogr.* **1979**, *12*, 387–394.

(3)   Slack, G. A. *J. Appl. Phys.* **1960**, *31*, 1571.

(4)   Messick, L.; Walker, W. C.; Glosser, R. *Phys. Rev. B* **1972**, *6*, 3941–3949.

(5)   Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261.

(6)   Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299–310.

(7)   Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866.

(8)   Alidoust, N.; Caspary Toroker, M.; Carter, E. A. *J. Phys. Chem. B* **2014**, *118*, 7963–71.

(9)   Dill, J. D.; Pople, J. A. *J. Chem. Phys.* **1975**, *62*, 2921.

(10)   Elp, J. Van; Eskes, H.; Kuiper, P.; Sawatzky, G. A. *Phys. Rev. B* **1992**, *45*, 1612–1622.

(11)   Kuiper, P.; Kruizinga, G.; Ghijsen, J.; Sawatzky, G. A.; Verweij, H. *Phys. Rev. Lett.* **1989**, *62*, 221–224.

(12)   Kerisit, S.; Rosso, K. M. *J. Chem. Phys.* **2007**, *127*, 124706.