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Enhancing magneto-ionic effects in cobalt oxide films by electrolyte engineering

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Further computational details.

Determination of the Hubbard U_{eff} term

The U_{eff} term of the Hubbard correction was determined by analyzing how this correction to DFT influences the material cell parameters as well as it localizes the unpaired electrons on the Co^{2+} cations. Results reported in Table S1 show that absence of Hubbard correction or low U_{eff} values leads to cell parameters that are closer to the X-ray determined ones. However, in these cases the spin density of Co^{2+} is partially delocalized. Increasing the U_{eff} term localizes the electron density on Co^{2+} but the optimized cell parameters become larger. An U_{eff} value of 3.0 eV appears to be a good compromise between spin density localization and cell parameters reproducibility and thus, it has been applied to all AIMD simulations. Remarkably, $U_{\text{eff}} = 3.0$ eV lies in between those suggested for Co_3O_4 in previous contributions.⁴⁻⁶

Table S1. Cell parameters and magnetization on the Co^{2+} tetrahedric sites as function of the applied Hubbard correction. Experimental values are added for comparison.

| Method (U_{eff} in eV) | a (Å) | μ (e^-) |
|----------------------------------|-------|-----------------|
| PBE-D3 | 8.06 | 2.24 |
| PBE-D3-U (U = 2.0) | 8.09 | 2.52 |
| PBE-D3-U (U = 2.5) | 8.09 | 2.57 |
| PBE-D3-U (U = 3.0) | 8.10 | 2.61 |
| PBE-D3-U (U = 3.5) | 8.10 | 2.64 |
| PBE-D3-U (U = 4.0) | 8.11 | 2.67 |
| Exp. | 8.08 | 3.00 |

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Model construction

The Co_3O_4 -propylene interface model was constructed through three successive steps. First of all, a slab model of Co_3O_4 was developed. The Co_3O_4 surface used is a (1x1) stoichiometric crystalline slab of the (110) facet. We chose the (110) facet as it has been shown to be the predominant surface in Co_3O_4 nanorods¹¹ and thus, it can be used as a representative example in the present simulations. The top outermost layer contains O^{2-} anions and Co^{3+} cations and, similarly to other Co_3O_4 slab models reported in the literature, the thickness of the model is around 10 Å and it implies 4 material layers.⁶ In a second step, 13 propylene carbonate molecules were added in the vacuum box between images. This leads to a solution with a solvent density of around 1.2 g cm⁻³, which is in agreement with the propylene carbonate density at room temperature. The initial conformation of the propylene carbonate solvent molecules was obtained with the Packmol software,¹² which creates initial configurations for MD simulations. Finally, a KX (X = Cl or I) unit was added to the model to account for the effect of the dissolved salt. The addition of one KX unit leads to solute concentrations of about 0.9 M. This value is higher than the concentration in experiments, but more dilute models are not feasible due to the required computational resources. Indeed, the final model already contains 283 atoms.

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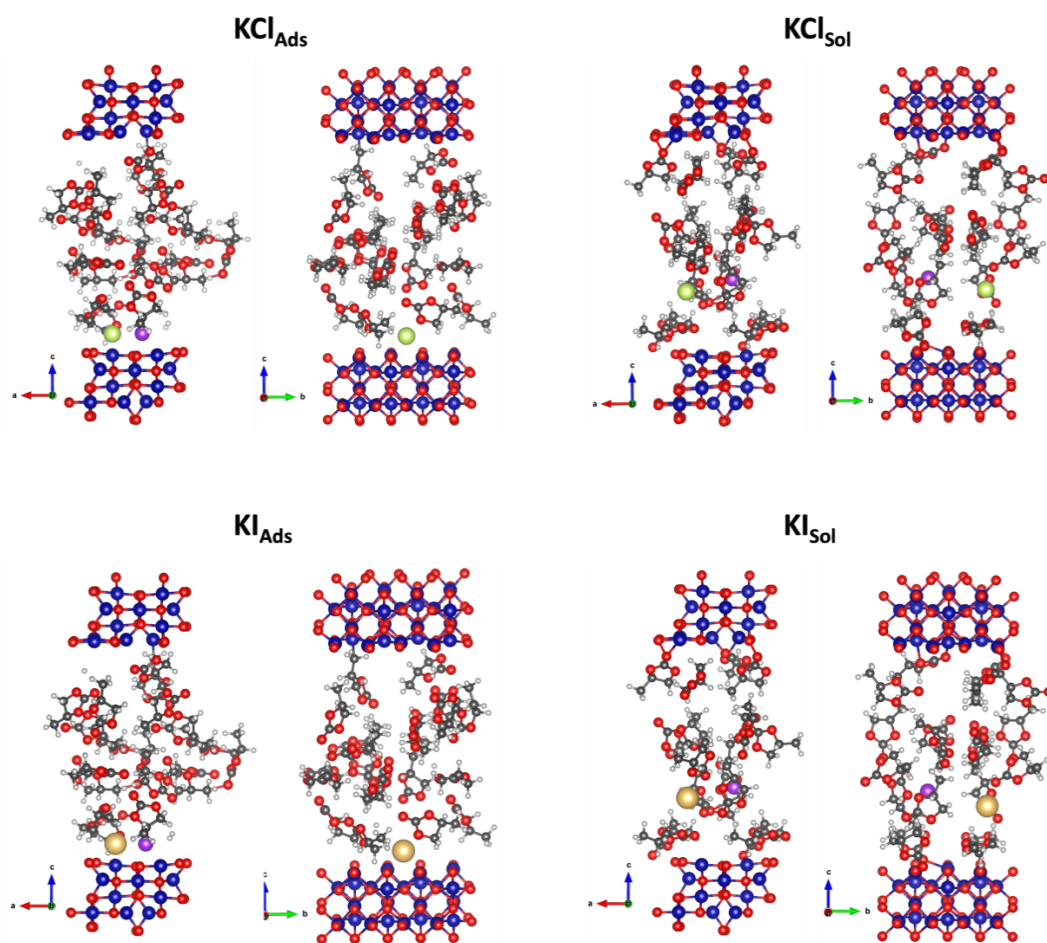


Fig. S1 Initial structures (two views) of the four AIMD simulations carried on. Label code: Co (blue), O (red), C (black), H (white), K (purple), Cl (green), I (pale orange).

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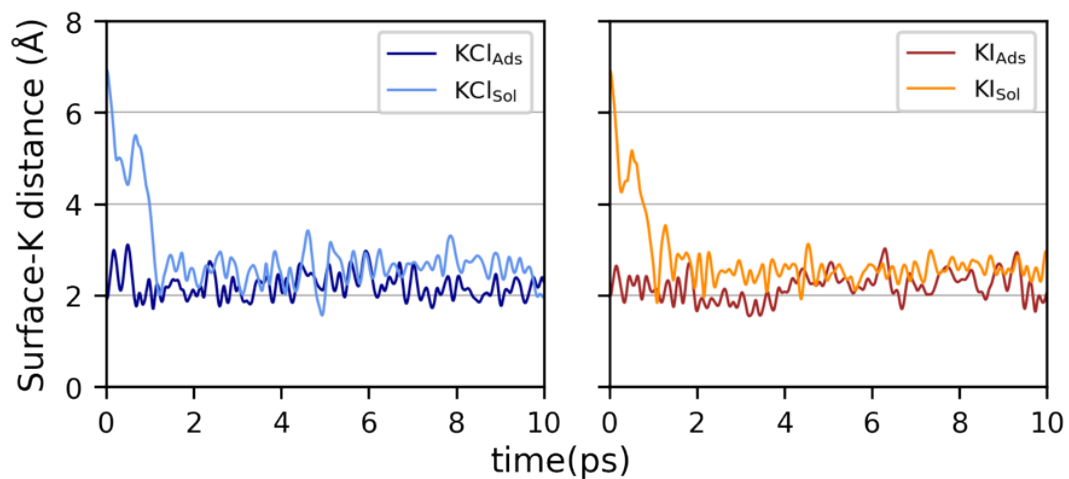


Fig. S2 Variation of the K···surface distance along the four AIMD simulations performed.

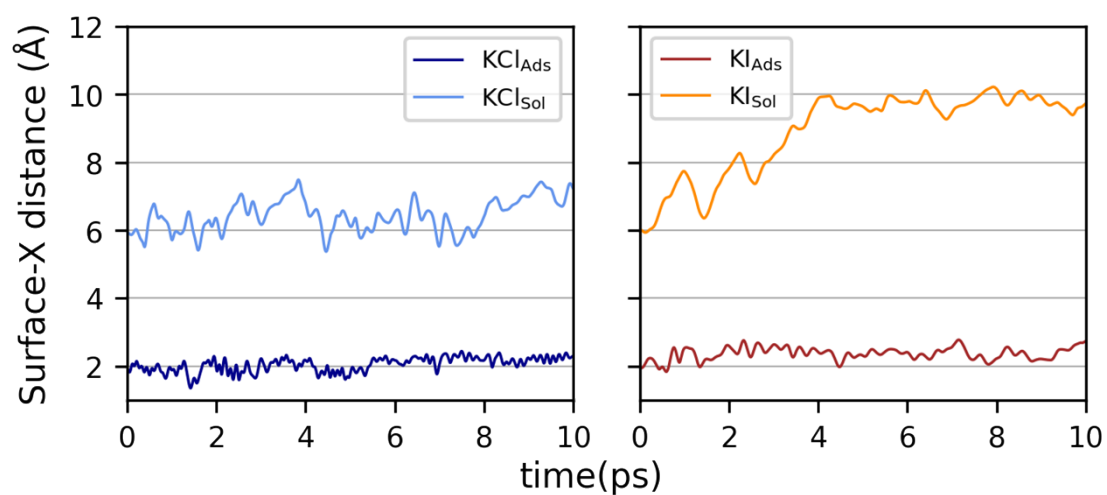


Fig. S3. Variation of the anion···surface distance along the four AIMD simulations performed.

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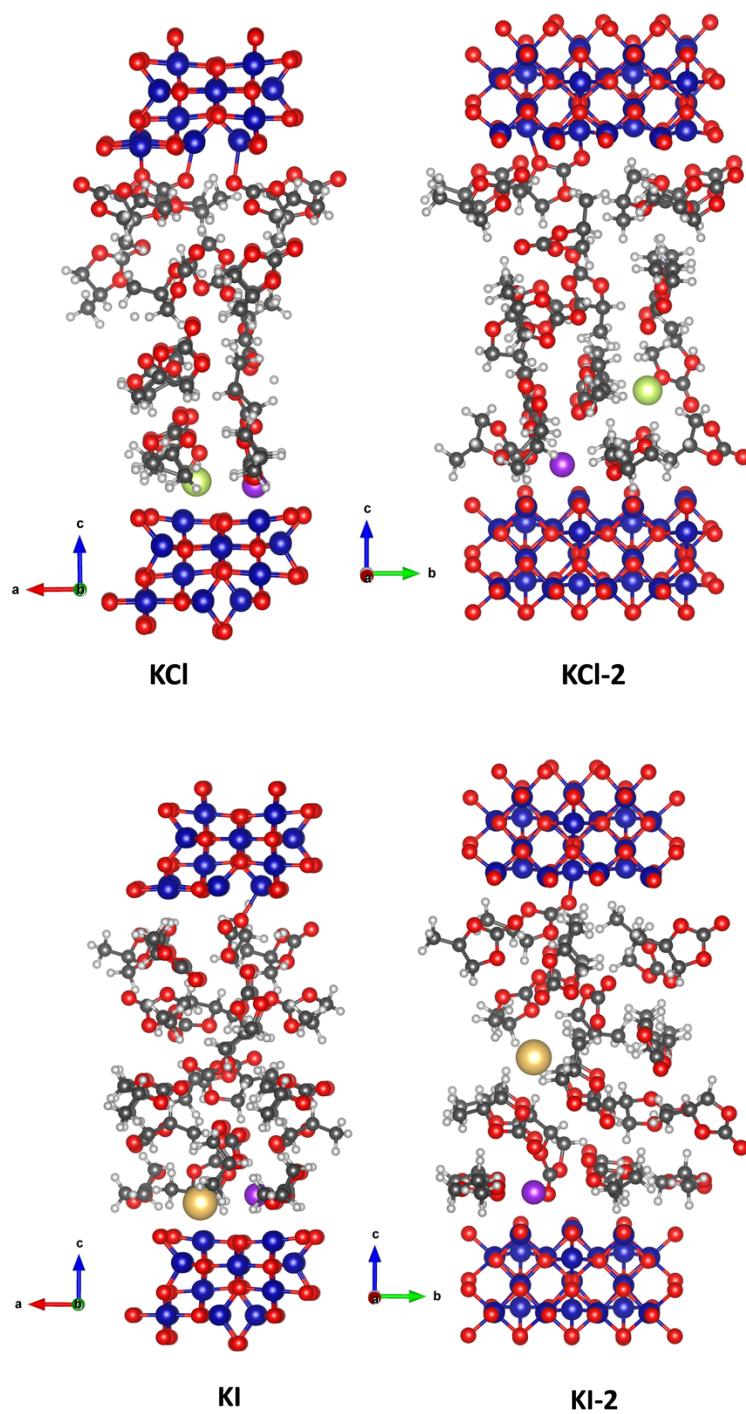


Fig. S4 Representative snapshots the four AIMD simulations. Label code: Co (blue), O (red), C (black), H (white), K (purple), Cl (green), I (pale orange).

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References

- (1) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865–3868.
- (2) S. Dudarev and G. Botton, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 1998, **57**, 1505–1509.
- (3) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104.
- (4) J. Chen, X. Wu, A. Selloni, *Phys. Rev. B* 2011, **83**, 245204.
- (5) D. Jiang, S. Dai, *Phys. Chem. Chem. Phys.* 2011, **13**, 978–984.
- (6) W. Hu, J. Lan, Y. Guo, X.-M. Cao, P. Hu, *ACS Catal.* 2016, **6**, 5508–5519.
- (7) W. G. Hoover, *Phys. Rev. A* 1985, **31**, 1695–1697.
- (8) S. A. Nosé, *J. Chem. Phys.* 1984, **81**, 511–519.
- (9) G. Kresse, J. Hafner, *Phys. Rev. B* 1993, **47**, 558–561.
- (10) G. Kresse, J. Furthmüller, *Phys. Rev. B* 1996, **54**, 11169–11186.
- (11) X. Xie, Y. Li, Z.-Q. Liu,; M. Haruta, W. Shen, *Nature* 2009, **458**, 746–749.
- (12) L. Martínez, R. Andrade, E. G. Birgin, J. M. Martínez, *J. Comput. Chem.* 2009, **30**, 2157–2164.