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Supporting Information

Enhanced Dissolution of Metal Oxides in Hydroxylated Solvents – Towards Application in Lithium-Ion Battery Leaching

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Enhanced dissolution of metal oxides in hydroxylated solvents – towards application in lithium-ion battery leaching

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EXPERIMENTAL

Chemicals and instrumentation

The metal oxides (MOs) studied in this work were cobalt (II) oxide (CoO, 95 wt.%), obtained from Alfa Aesar, nickel (II) oxide (NiO, 99 wt.%) and manganese (II) oxide (MnO, 99 wt.%) from Sigma-Aldrich. Lithium nickel manganese cobalt oxide ($LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$, ≥ 98 wt.%) was used as NMC active cathode material powder, obtained from Sigma-Aldrich. Glycerol (Gly, 99 wt.%) and ethylene glycol (EG, ≥ 99 wt.%) were obtained from Fisher whilst 1,3-butanediol (BdOH, ≥ 99 wt.%) was acquired from Sigma-Aldrich and 1-butanol (BuOH, ≥ 99 wt.%) from Prolabo. The acids hydrochloric acid (HCl, 37 wt.%) and trifluoromethanesulfonic acid (TFMS, 98 wt.%) were purchased from Fisher and Sigma-Aldrich, respectively. Lactic acid (LA, 85 wt.%) was acquired from Acros Organics. The metal salts used for UV-Vis experiments, cobalt (II) chloride hexahydrate (99 wt. %) and lithium chloride (99 wt. %) were obtained from Merck.

UV-Vis spectroscopy was used to determine the cobalt cation speciation in aqueous or solvent-based media. The absorption spectra of $CoCl_2 \cdot 6H_2O$ dissolved in chloride-rich media, with $LiCl$ as a chloride source, was determined between 300-800 nm in a microplate reader (Synergy HT, Biotek, USA). The chemical structures of the solvent-based media before and after undergoing 40 °C for 72 h were confirmed by NMR spectroscopy using a Bruker Avance (300 MHz for ^1H and 75.5 MHz for ^{13}C) at room temperature, with deuterated water (D_2O) or dimethyl sulfoxide (DMSO) as solvents and trimethylsilylpropanoic acid (TSP) as the reference.

Metal concentrations were determined using a Picofox S2 (Bruker) total reflection X-ray fluorescence (TXRF) spectrometer, with a molybdenum X-ray source. The voltage of the X-ray tube was 50 kV and the current 600 μA. Initially, sample carriers were pre-treated with 10 μL of silicon in isopropanol solution and dried on a hot plate at 60 °C for at least 15 min. Samples were prepared by diluting an aliquot of the metal-containing solutions from the solubility assays in 0.2 wt.% poly(vinyl alcohol) (PVA, Sigma-Aldrich, average molecular weight 30,000-70,000 $g.mol^{-1}$, 87-90 wt.% hydrolyzed), with yttrium (Y) as an internal standard (1000 ppm Certipur® standard, Sigma-Aldrich). Gallium (Ga) was used on each measurement session as a quality control of the sensitivity of the instrument. Before acquisition, which was carried out for 120 s, 10 μL of the sample were added onto a pre-treated carrier and dried on a hot plate at 60 °C for at least 15 min.

Metal oxide dissolution and characterization

Table S1. Composition of acidic aqueous or hydroxylated-based solvent systems used in the dissolution of metal oxides.

Composition	[Acid] (M)	Solvent content (v/v %)	Water content (v/v %)
HCl + Water	0.5; 1.0; 2.0	-	94-98
HCl + Gly	0.5; 1.0; 2.0	82-95	3.0-12
HCl + EG	0.5; 1.0; 2.0	82-95	3.0-12
HCl + BdOH	0.5; 1.0; 2.0	82-95	3.0-12
HCl + BuOH	0.5; 1.0; 2.0	82-95	3.0-12
TFMS + Water	1.0	-	91
TFMS + EG	1.0	91	0.31
LA + Water	1.0	-	92
LA + EG	1.0	91	1.6
HCl + Gly/Water mixture	1.0	5.5; 25; 48; 71	91; 72; 49; 26
HCl + EG/Water mixture	1.0	5.1; 25; 50; 70	90; 70; 45; 25

LITERATURE DATA

Table S2. Ecotoxicity, toxicity and cost parameters of the four hydroxylated solvents studied in this work.

Hydroxylated solvent	Ecotoxicity[a] (M)	Toxicity[b] (g/kg-day)	Cost[c] (€/tonne)
Glycerol (Gly)	0.164	126	231
Ethylene Glycol (EG)	0.176	4.70	139
1,3-butanediol (BdOH)	0.114	186	416
1-butanol (BuOH)	< 0.020	0.79	508

[a]Effective concentration value (EC_{50}), designated as affecting the growth of *L.* gibba, after exposure to these solvents in ranges of 0 to 400 mM for BdOH and BuOH and 0 to 500 mM for Gly and EG, over 7 days. Data obtained from ref. 44 from the main manuscript.

[b]Median lethal dose (LD_{50}) of oral intake in rats, using latest data from the United States Environmetal Protection Agency CompTox Chemicals Dashboard.

[c]Lowest commercial cost found from online wholesalers as of January 2023.

RESULTS

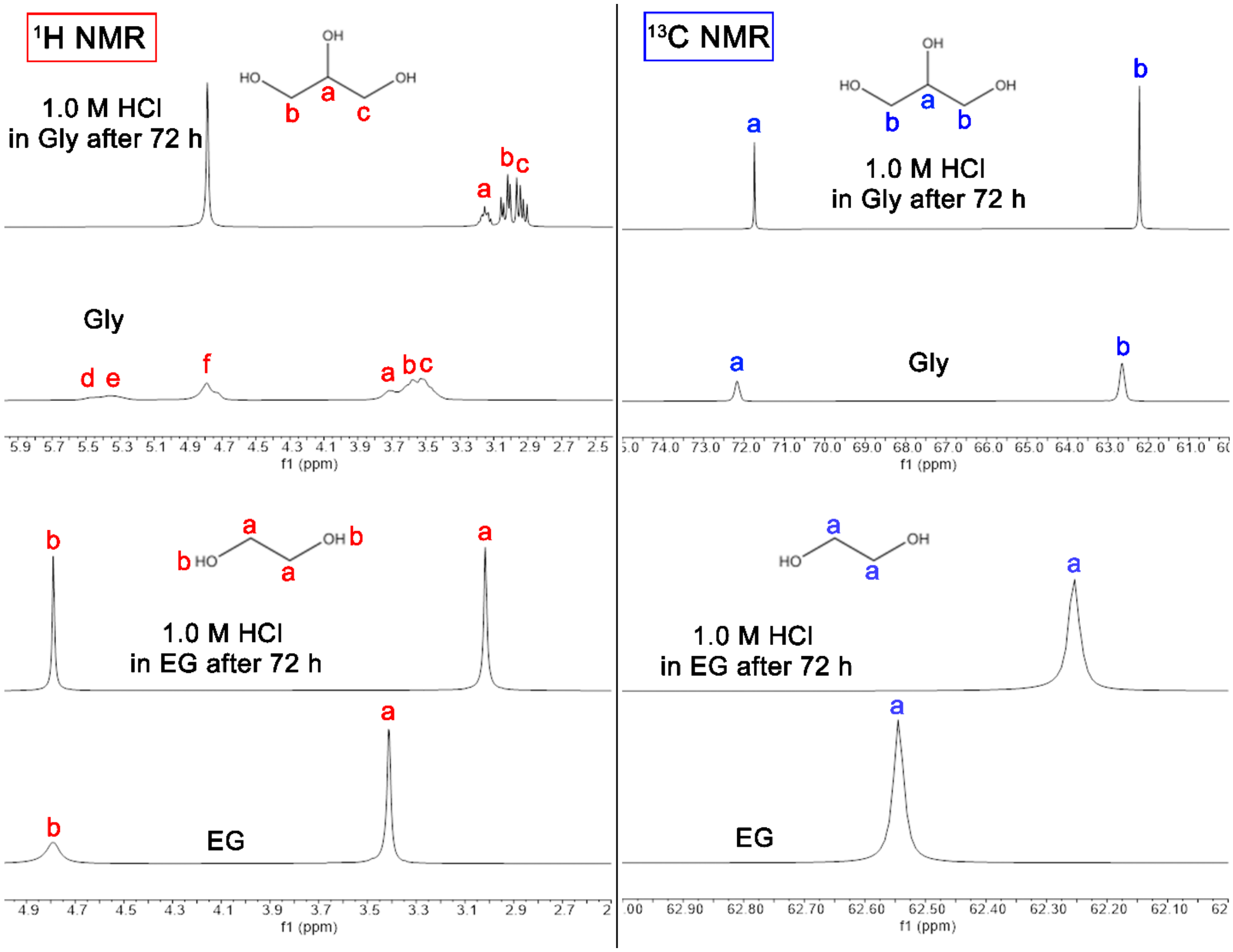

Figure S1. ^{1}H- (**left**) and ^{13}C-NMR (**right**) spectra of pure Gly or EG and 1.0 M HCl in these solvents after 72 h of continuous stirring at 40 °C.

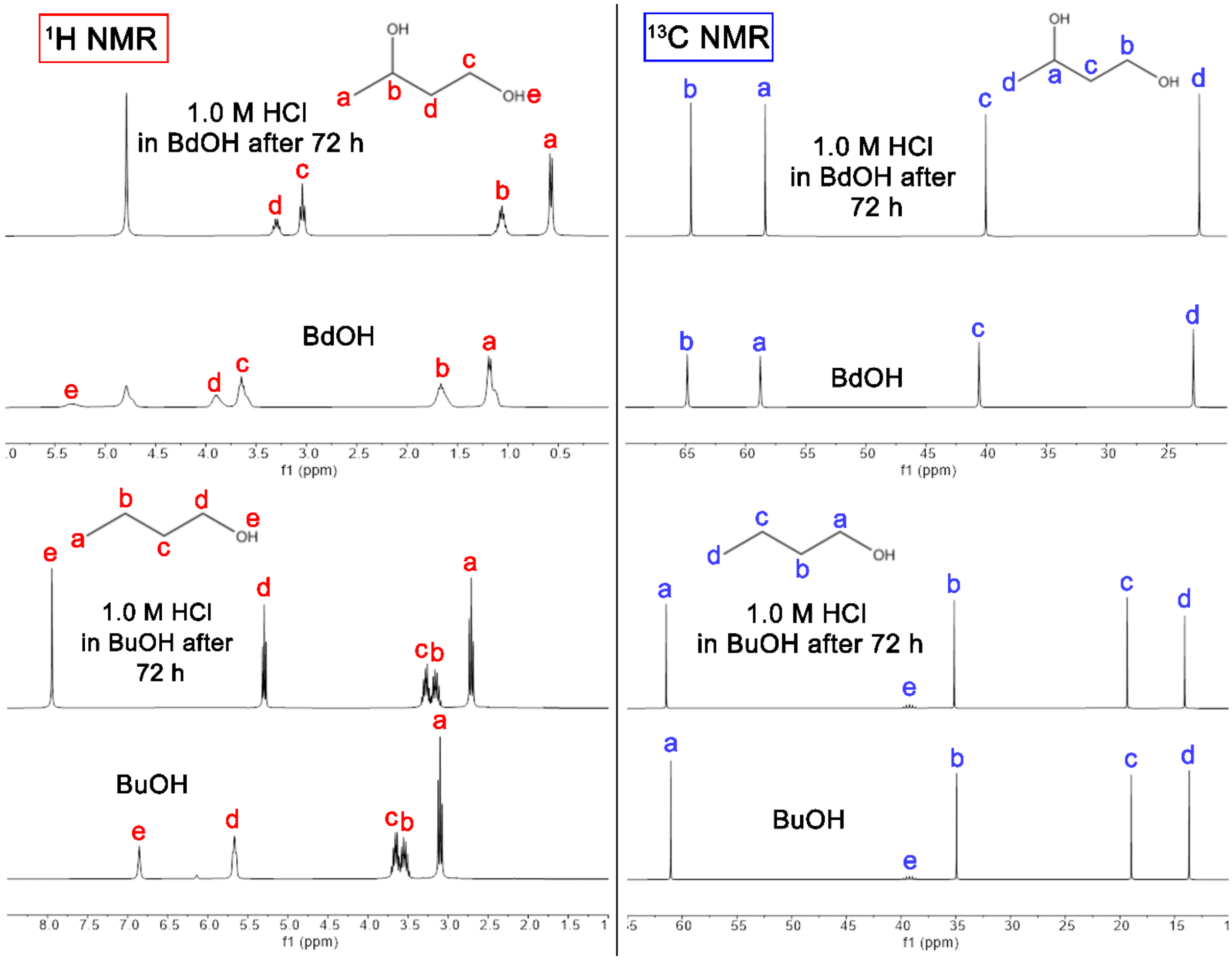

Figure S2. ^{1}H- (**left**) and ^{13}C-NMR (**right**) spectra of pure BdOH or BuOH and 1.0 M HCl in these solvents after 72 h of continuous stirring at 40 °C.

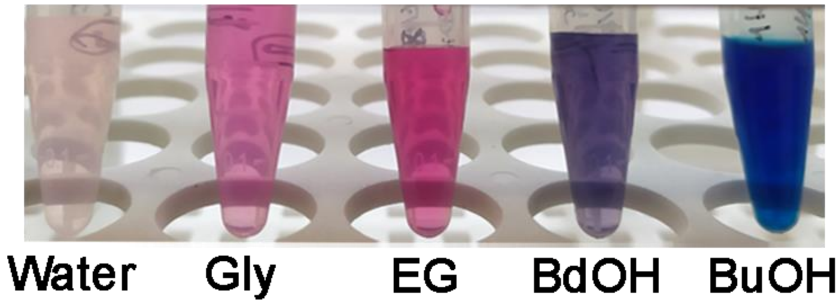

Figure S3. Photo of the solutions after CoO dissolution for 72 h of continuous stirring at 2,000 rpm and 40 °C in 1.0 M HCl systems.

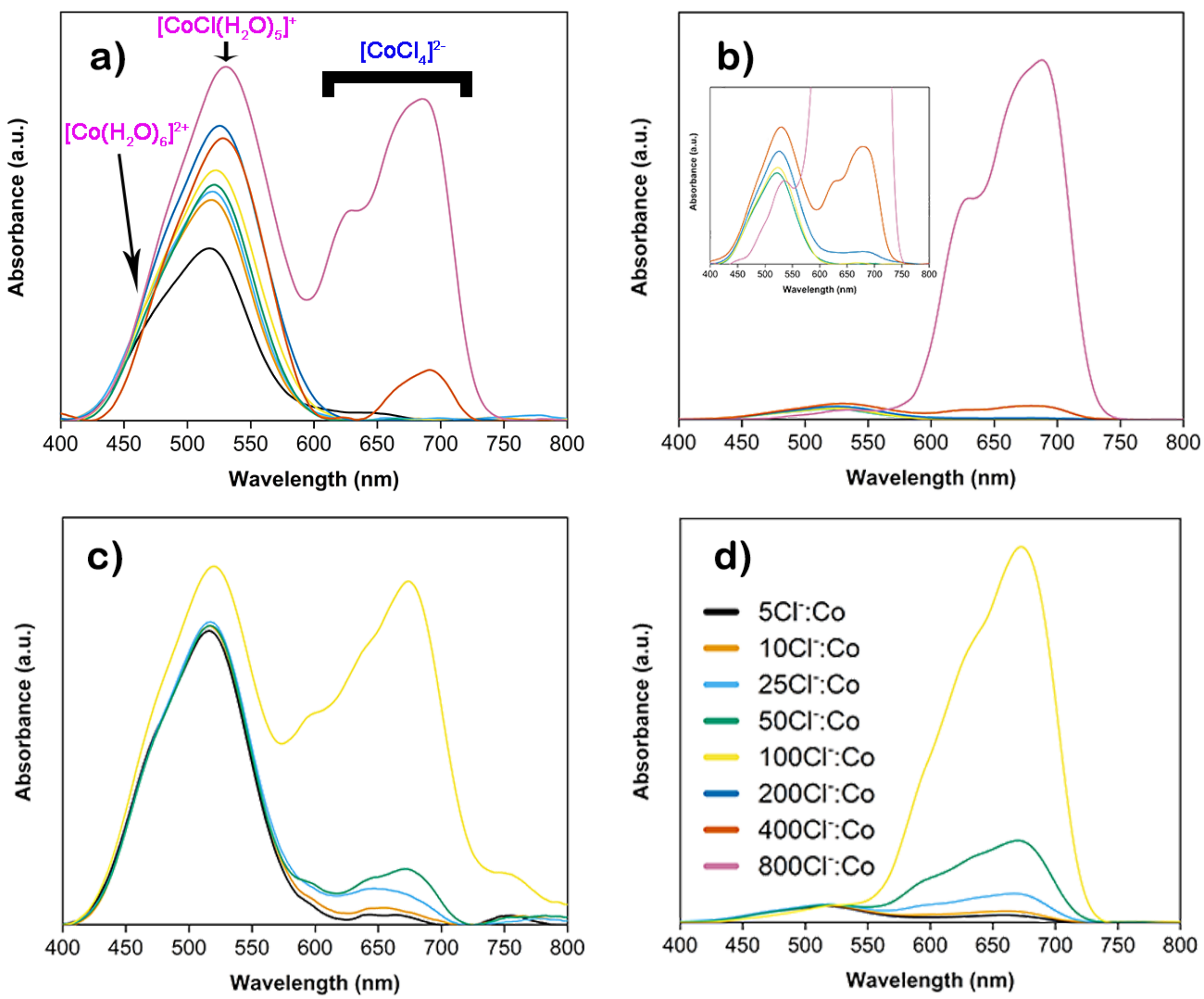

Figure S4. UV-Vis spectra of $CoCl_2 \cdot H_2O$ in glycerol (a), ethylene glycol (b), 1,3-butanediol (c) or 1-butanol (d), depending on the chloride:cobalt molar ratio involved. The chloride source in these solutions was LiCl. The three possible cobalt species are depicted in graph **a)**. The legend depicted in graph d) applies to all graphs in the Figure. In graph b), an inset was provided with a closer look at the differences between chloride and cobalt molar ratios in EG.

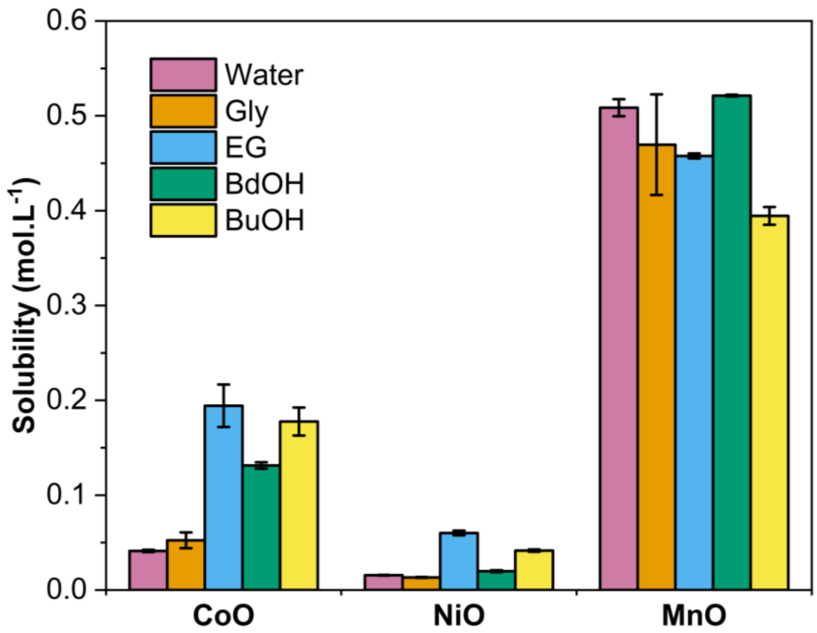

Figure S5. Solubility of CoO, NiO and MnO in 1.0 M HCl aqueous or solvent-based solutions, after 72 h of continuous stirring for 2,000 rpm at 40 °C.

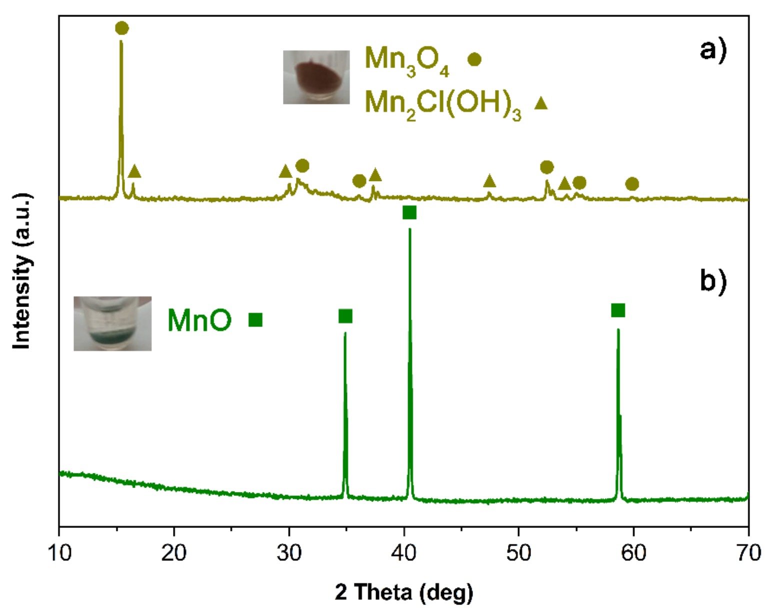

Figure S6. XRD spectra of the remaining MnO powder **a)** after leaching in 1.0 M HCl BuOH solution for 72 h of continuous stirring at 2,000 rpm and 40 °C, and **b)** MnO powder, before leaching. The respective powder image is provided as an inset, next to the identified species in each of them.

Table S3. Parameters of the kinetics model based on the shrinking core model, logarithmic rate and mixed kinetics equation fittings (**Figures S7 and S8**) for Co, Ni and Mn at different reaction temperatures (25 °C, 40 °C and 60 °C). These values consider the leaching of these three metals from a NMC matrix, for at least 8 h in 0.5 M HCl in 25% Gly/Water.

		Co		**Ni**		**Mn**	
	T (°C)	k (h^{-1})	R^2	k (h^{-1})	R^2	k (h^{-1})	R^2
Diffusion-controlled (Eq. 5)	25	0.002	0.84	0.002	0.76	0.005	**0.94**
	40	0.003	0.87	0.003	0.74	0.012	**0.97**
	60	0.022	0.92	0.015	0.96	0.038	**0.96**
Surface-controlled (Eq. 6)	25	0.008	0.60	0.008	0.56	0.015	0.74
	40	0.017	0.65	0.017	0.57	0.038	0.86
	60	0.073	0.95	0.059	0.92	0.119	0.96
Logaritmic-rate (Eq. 8)	25	0.021	0.91	0.024	0.84	0.129	0.97
	40	0.052	0.94	0.048	0.83	1.429	0.82
	60	0.653	0.64	0.289	0.88	0.702	0.97
Mixed-kinetics (Eq. 9)	25	0.001	0.92	0.001	0.86	0.010	0.96
	40	0.003	0.95	0.003	0.84	0.197	0.79
	60	0.050	0.58	0.019	0.85	0.049	0.96

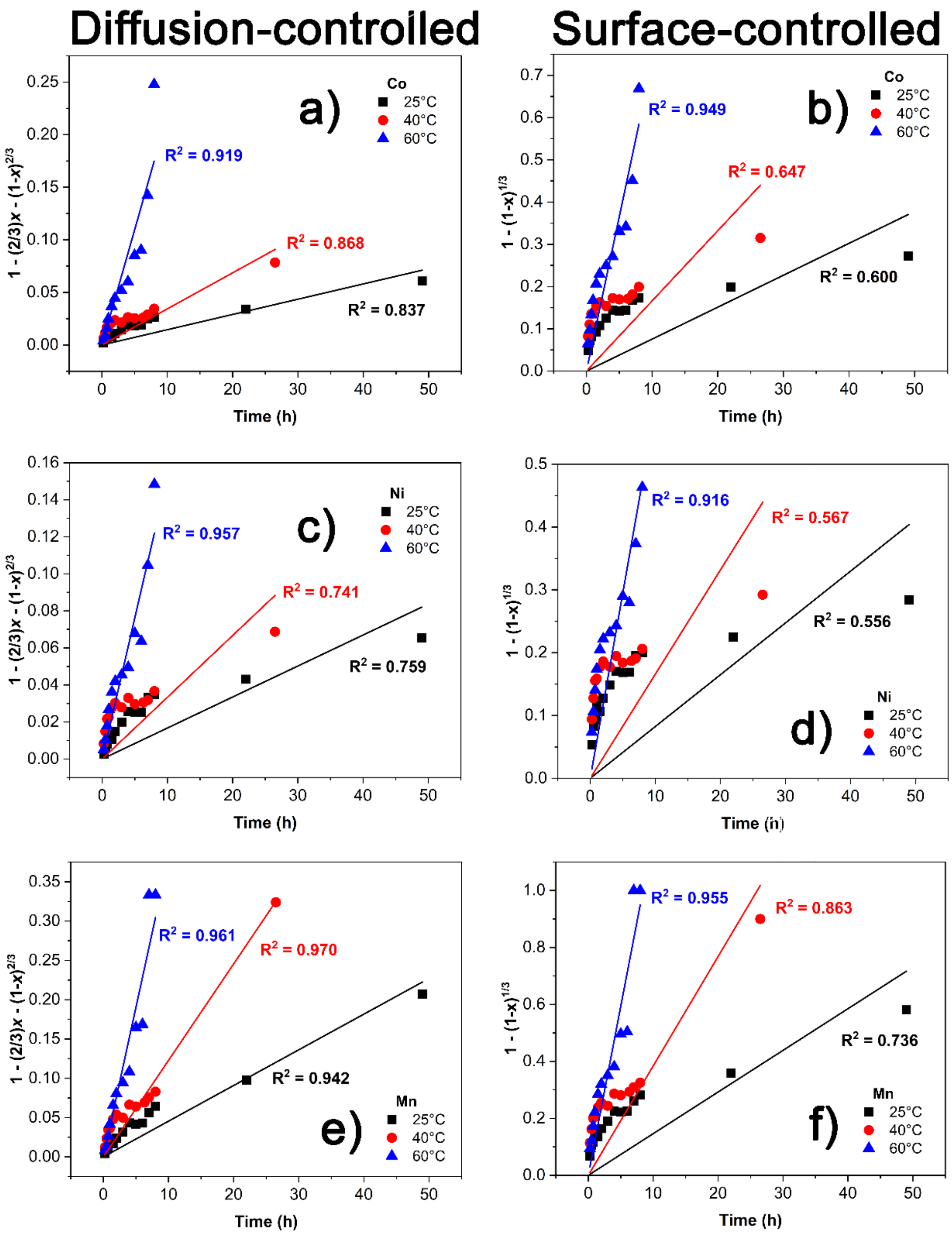

Figure S7. Fittings of the shrinking core kinetic model equations for Co (**a,b**), Ni (**c,d**) and Mn (**e,f**) at different reaction temperatures (25 °C, 40 °C and 60 °C). These fittings were carried out for both a diffusion-controlled process and a surface controlled chemical reaction. These values consider the leaching of these three metals from a NMC matrix, for at least 8 h in 0.5 M HCl in Gly + Water (25% v/v Gly).

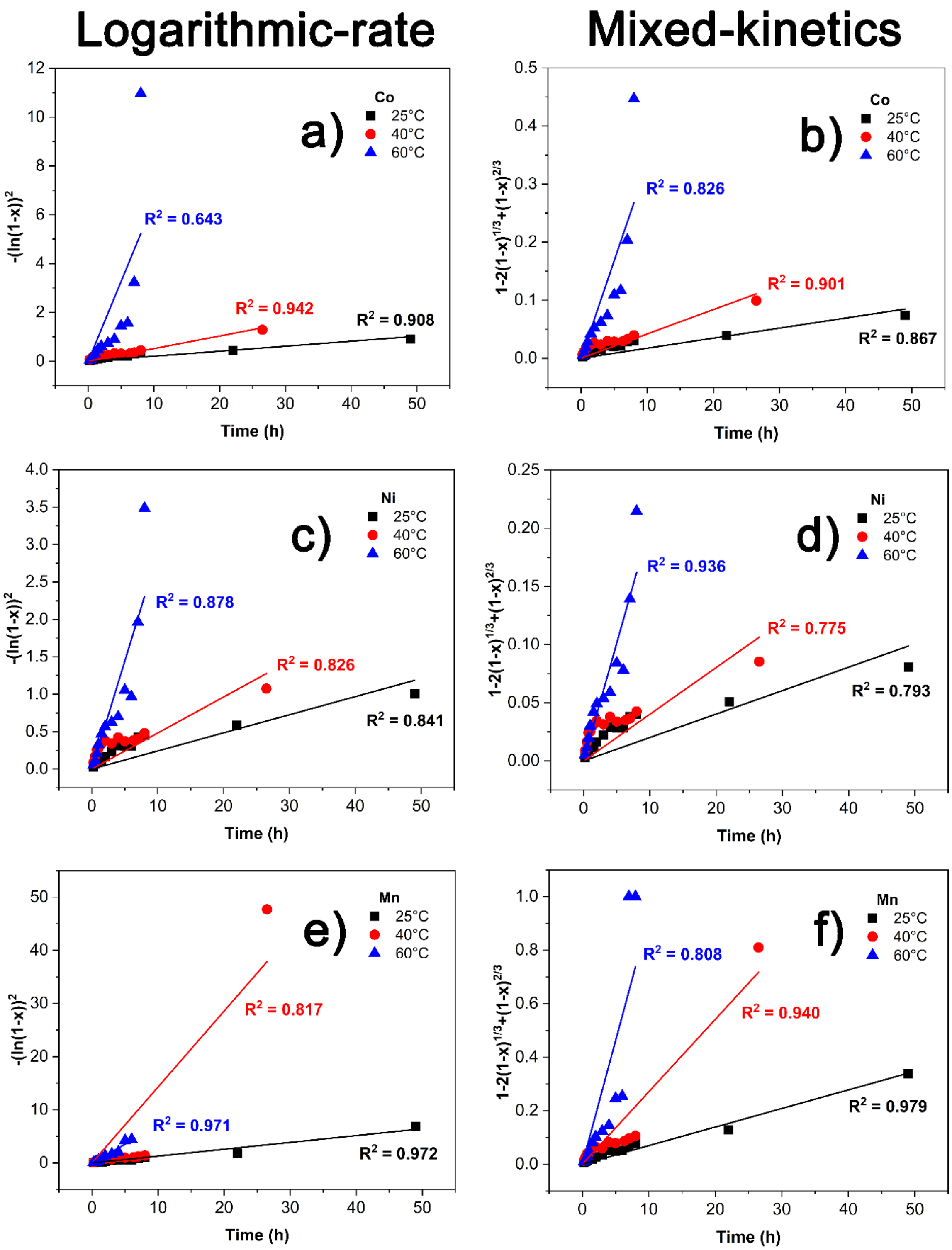

Figure S8. Fittings of the logarithmic rate and mixed-kinetic model equations for Co (**a,b**), Ni (**c,d**) and Mn (**e,f**) at different reaction temperatures (25 °C, 40 °C and 60 °C). These values consider the leaching of these three metals from a NMC matrix, for at least 8 h in 0.5 M HCl in Gly + Water (25% v/v Gly).

Table S4. Parameters of the kinetics model based on the shrinking core model equation fittings (diffusion- and surface reaction-controlled) (**Figure S9**) for Co and Ni at different reaction temperatures (25 °C, 40 °C and 60 °C). A two-step process was considered, with 1 and 2 describing the first and second step of the leaching process, respectively, as subscripts in the reaction rate constant *k*. These values consider the leaching of these metals from a NMC matrix, for at least 8 h in 0.5 M HCl in 25% Gly/Water.

		Co				**Ni**			
	T (°C)	k_1 (h^{-1})	R^2	k_2 (h^{-1})	R^2	k_1 (h^{-1})	R^2	k_2 (h^{-1})	R^2
Diffusion-controlled (Eq. 5)	25	0.005	**0.96**	0.001	0.97	0.007	**0.96**	0.001	0.96
	40	0.016	**0.96**	0.002	0.98	0.022	**0.96**	0.002	0.96
	60	0.023	**0.99**	0.035	0.76	0.023	**0.99**	0.019	0.83
Surface-controlled (Eq. 6)	25	0.046	0.85	0.003	0.96	0.054	0.86	0.002	0.94
	40	0.132	0.90	0.007	0.98	0.152	0.90	0.005	0.96
	60	0.135	0.96	0.064	0.81	0.159	0.97	0.037	0.84

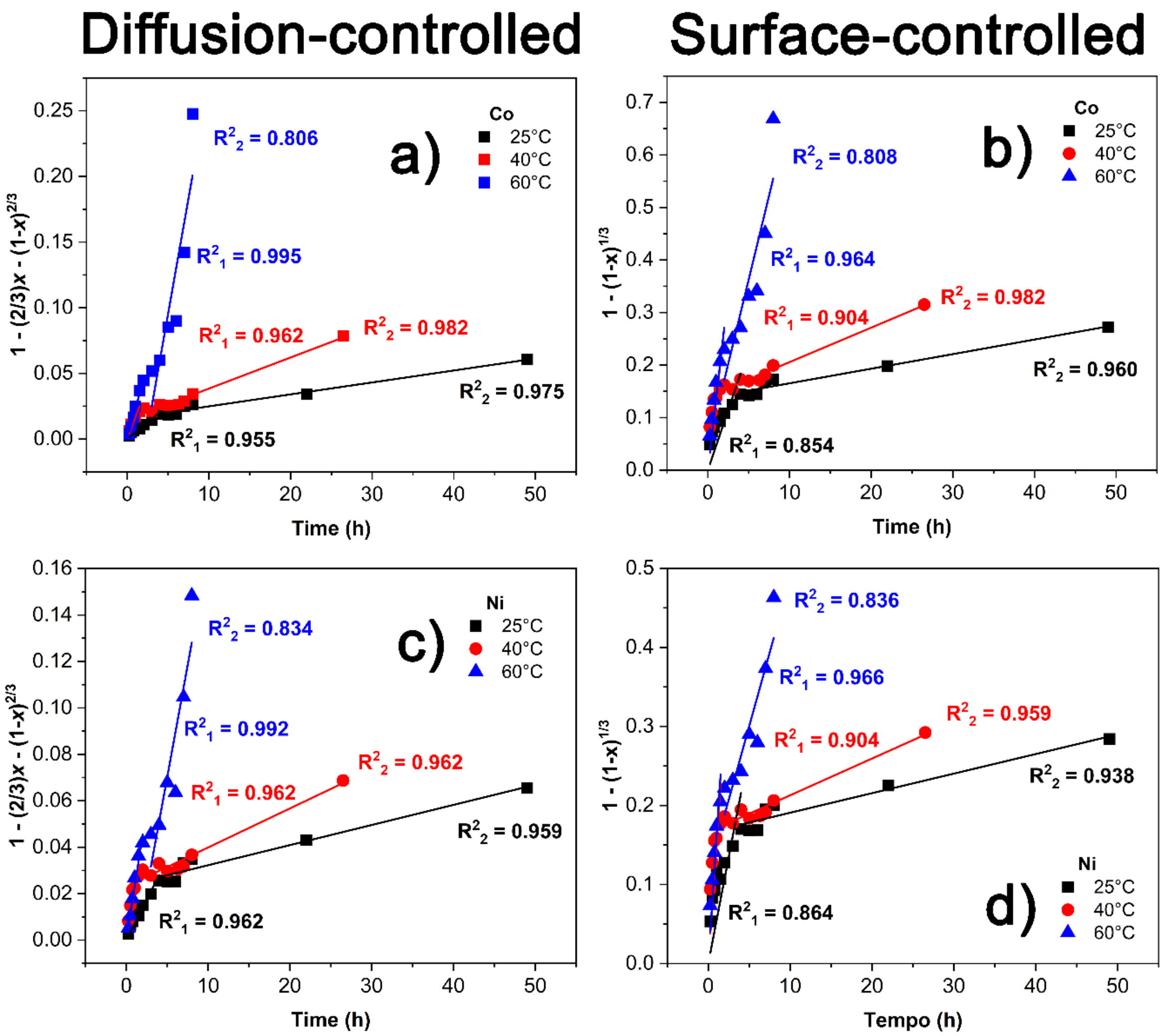

Figure S9. Fittings of the shrinking core kinetic model equations for Co (**a,b**) and Ni (**c,d**) at different reaction temperatures (25 °C, 40 °C and 60 °C). These fittings were carried out for both a diffusion-controlled process and a surface controlled chemical reaction, in a two-step process (1 and 2 as subscripts in the correlation coefficient R^2). These values consider the leaching of these metals from a NMC matrix, for at least 8 h in 0.5 M HCl in Gly + Water (25% v/v Gly).