Electronic Supplementary Information for

"An X-ray absorption spectroscopy investigation of the coordination environment of electrogenerated Ni(II)-pseudohalide complexes arising from the anodic polarization of Ni electrodes in DMSO solutions of NCO^-, NCS^- and $NCSe^-$ ions"

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Table S1. Parameters used to fit the NiO powder standard ('Sample 1'), shown in Figure 2 and Figure S1.

# parameters	6
Independent points	27.6
k-range	2.0 – 13.0
R-range	1.0 – 5.0
k-weights used	1, 2, 3
Reduced χ^2	750
ΔE_0 [eV]	-0.97 ± 0.57
amp (S_0^2)	0.78 ± 0.07
ss1a (σ^2 for first single scattering path, Ni-O)	0.0036 ± 0.0019
ss1 (σ^2 for subsequent single scattering paths)	0.0029 ± 0.0005
ss (σ^2 for multiple scattering paths)	0.0035 ± 0.0005
scale (for each path, $\Delta r = r*scale$)	0.0020 ± 0.0010

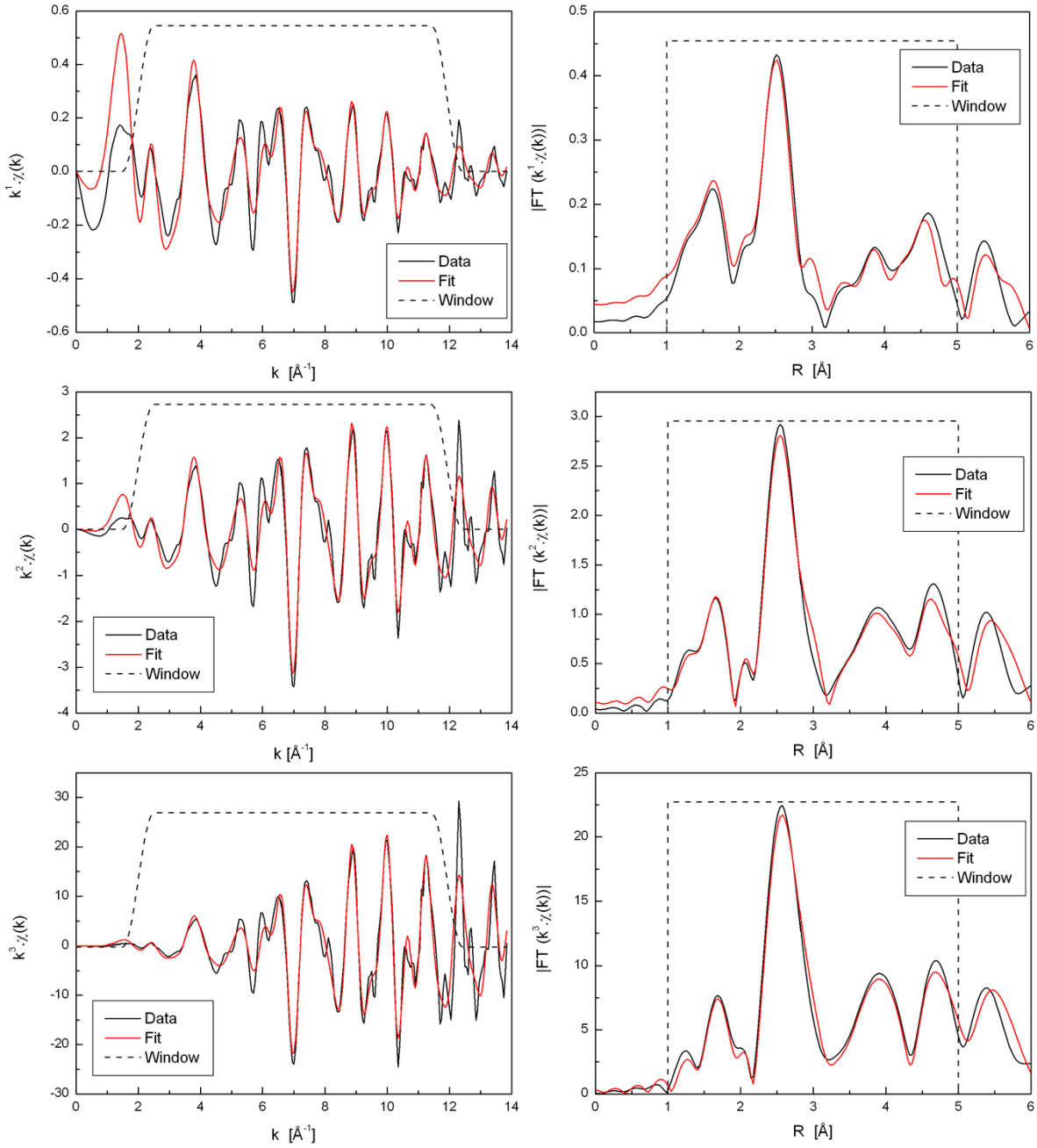

Figure S1. NiO powder standard ('Sample 1') EXAFS data (black lines) and fits (red lines) in k-space (left) and R-space (right) for various k-weightings: k^1 (top), k^2 (middle), k^3 (bottom). The data ranges used for fitting are shown by the window functions (black dashed lines).

Table S2. Parameters used to fit the Ni^{2+} in H_2O standard ('Sample 2'), shown in Figure 3 and Figure S2.

# parameters	7
Independent points	24.7
k-range	2.0 – 11.85
R-range	1.0 – 5.0
k-weights used	1, 2, 3
Reduced χ^2	58
ΔE_o [eV]	-2.17 ± 0.37
amp (S_o^2), 1st path	4.00 ± 0.15
r, 1st path	2.054 ± 0.004
ss, 1st path	0.0023 ± 0.0006
amp (S_o^2), 2nd path	5.75 ± 1.59
r, 2nd path	4.070 ± 0.026
ss, 2nd path	0.023 ± 0.011

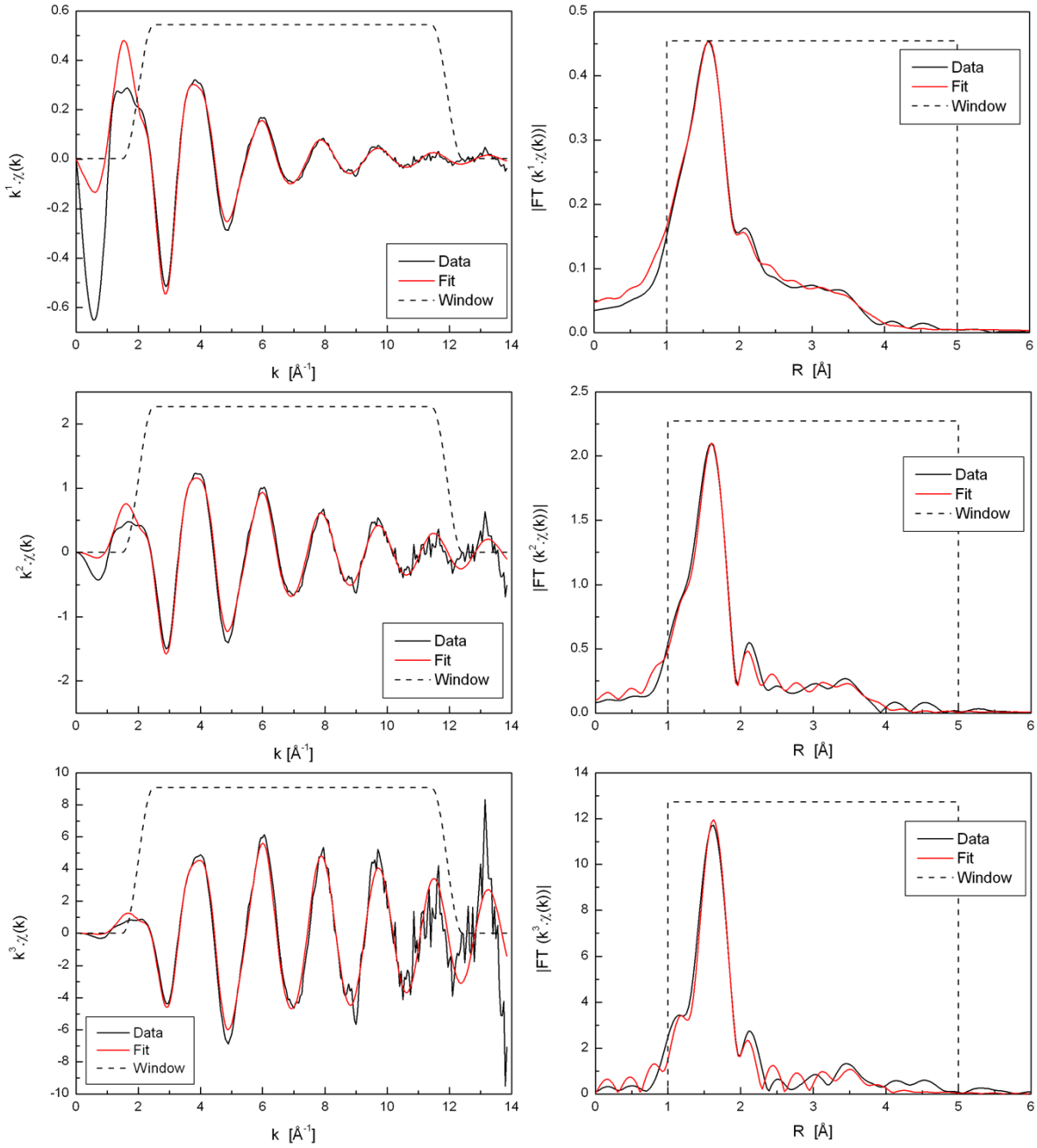

Figure S2. $Ni(NO_3)_2$ in H_2O ('Sample 2') EXAFS data (black lines) and fits (red lines) in k-space (left) and R-space (right) for various k-weightings: k^1 (top), k^2 (middle), k^3 (bottom). The data ranges used for fitting are shown by the window functions (black dashed lines).

Table S3. Parameters used to fit the Ni^{2+} in DMSO standard ('Sample 3'), shown in Figure 4 and Figure S3.

# parameters	9
Independent points	20.0
k-range	2.0 – 10.0
R-range	1.0 – 5.0
k-weights used	1, 2, 3
Reduced χ^2	111
ΔE_0 [eV]	-4.51 ± 0.56
amp (S_0^2), O path	4.14 ± 0.21
r, O path	2.053 ± 0.006
ss, all paths	0.0039 ± 0.0009
amp (S_0^2), S path	2.10 ± 0.27
r, S path	3.165 ± 0.011
amp (S_0^2), C paths	4.61 ± 0.65
r, C_1 path	3.948 ± 0.029
r, C_2 path	4.157 ± 0.031

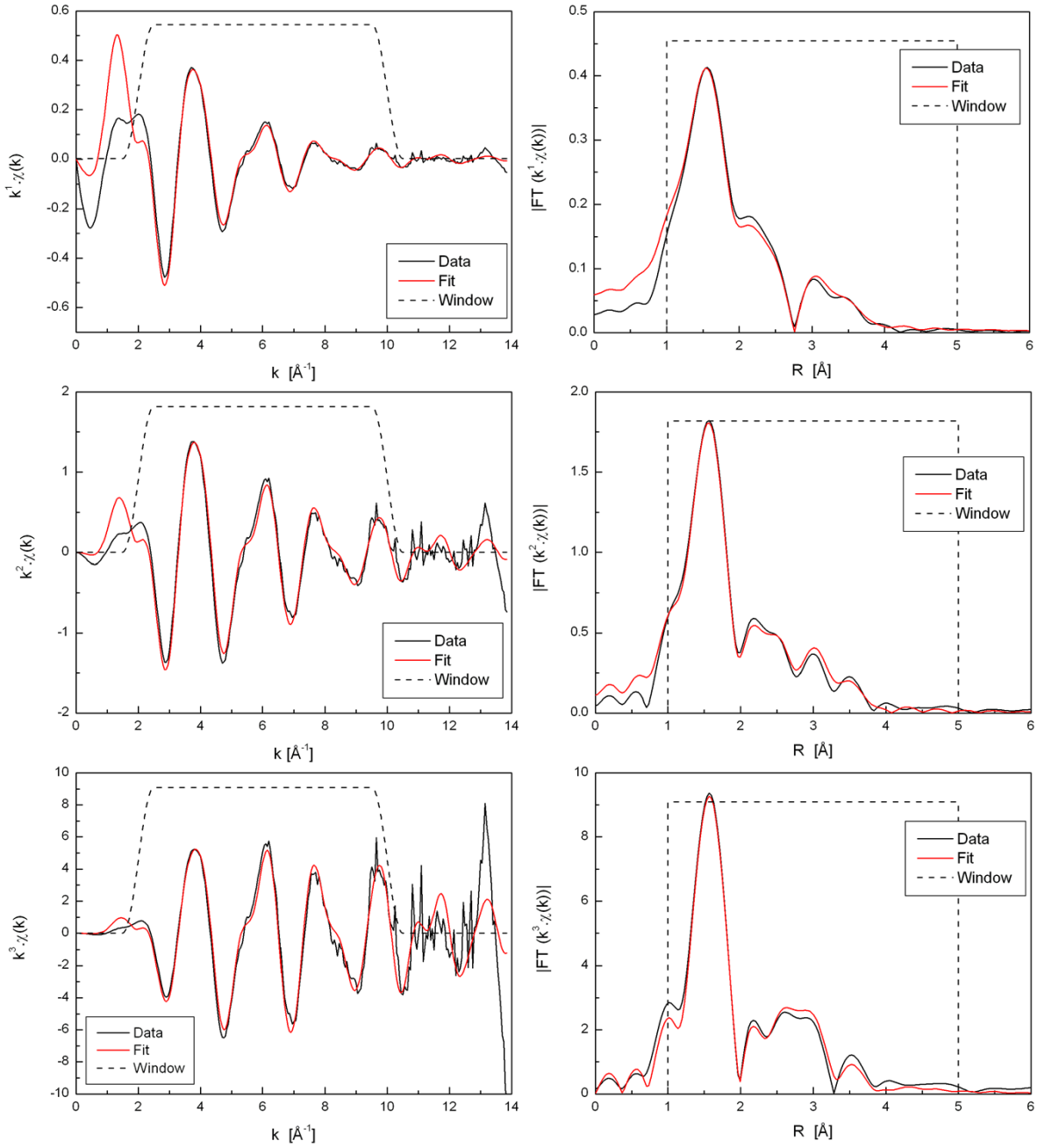

Figure S3. $Ni(NO_3)_2$ in DMSO ('Sample 3') EXAFS data (black lines) and fits (red lines) in k-space (left) and R-space (right) for various k-weightings: k^1 (top), k^2 (middle), k^3 (bottom). The data ranges used for fitting are shown by the window functions (black dashed lines).

Table S4. Parameters used in single-scattering fits for NCX^- coordinated to a Ni(II) centre (X=O, S, and Se), shown in Figures S4-S7.

Parameter	X = O	X = S	X = Se	echem X = O
# parameters	13	13	13	13
Independent points	20.0	20.0	20.0	20.0
k-range	2.0 – 10.0	2.0 – 10.0	2.0 – 10.0	2.0 – 10.0
R-range	1.0 – 5.0	1.0 – 5.0	1.0 – 5.0	1.0 – 5.0
k-weights used	1, 2, 3	1, 2, 3	1, 2, 3	1, 2, 3
Reduced χ^2	126	232	253	34.4
ΔE_0 (all paths)	-5.6 ± 1.3	-6.2 ± 1.2	-5.6 ± 2.2	-6.9 ± 1.5
σ^2 (DMSO paths)	0.006 ± 0.006	0.003 ± 0.002	0.003 ± 0.003	0.006 ± 0.010
σ^2 (NCX^- paths)	0.003 ± 0.019	0.001 ± 0.008	0.008 ± 0.009	0.001 ± 0.015
scale (DMSO)[a]	0.65 ± 0.24	0.64 ± 0.11	0.61 ± 0.18	0.60 ± 0.26
amp_S (DMSO)	1.69 ± 1.01	2.19 ± 0.44	1.58 ± 1.17	1.62 ± 1.31
amp (NCX^-)	0.95 ± 1.13	1.25 ± 0.74	1.58 ± 1.17	0.82 ± 0.92
r_O (DMSO)	2.047 ± 0.127	2.014 ± 0.017	2.041 ± 0.041	2.042 ± 0.066
r_S (DMSO)	3.147 ± 0.024	3.132 ± 0.016	3.134 ± 0.023	3.118 ± 0.025
r_C1 (DMSO)	3.939 ± 0.056	3.927 ± 0.046	3.955 ± 0.065	3.963 ± 0.059
r_C2 (DMSO)	4.163 ± 0.073	4.102 ± 0.058	4.127 ± 0.092	4.152 ± 0.082
r_N (NCX^-)	2.073 ± 0.352	2.155 ± 0.048	2.098 ± 0.181	2.033 ± 0.156
r_C (NCX^-)	2.735 ± 0.093	2.709 ± 0.041	2.817 ± 0.097	2.693 ± 0.098
r_X (NCX^-)	4.438 ± 0.112	4.632 ± 0.045	4.848 ± 0.061	4.431 ± 0.109

[a] For the DMSO paths, amp(O) = scale*4.14, amp(C) = scale*4.61.

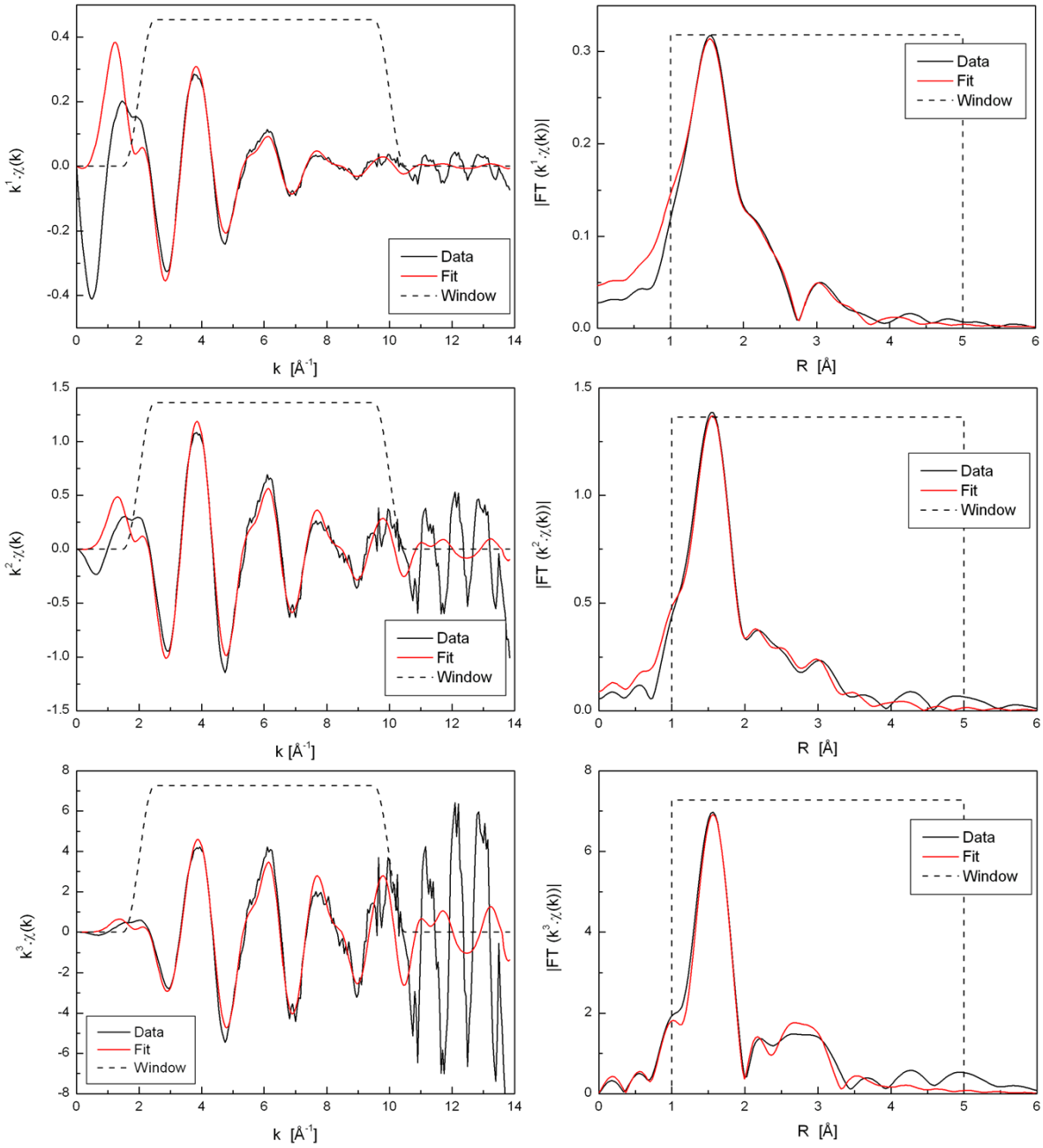

Figure S4. Ni-NCO 2:1 KOCN:Ni^{2+} mole ratio model solution in DMSO ('Sample 4'), fitted using a single shell model. EXAFS data (black lines) and fits (red lines) in k-space (left) and R-space (right) for various k-weightings: k^1 (top), k^2 (middle), k^3 (bottom). The data ranges used for fitting are shown by the window functions (black dashed lines).

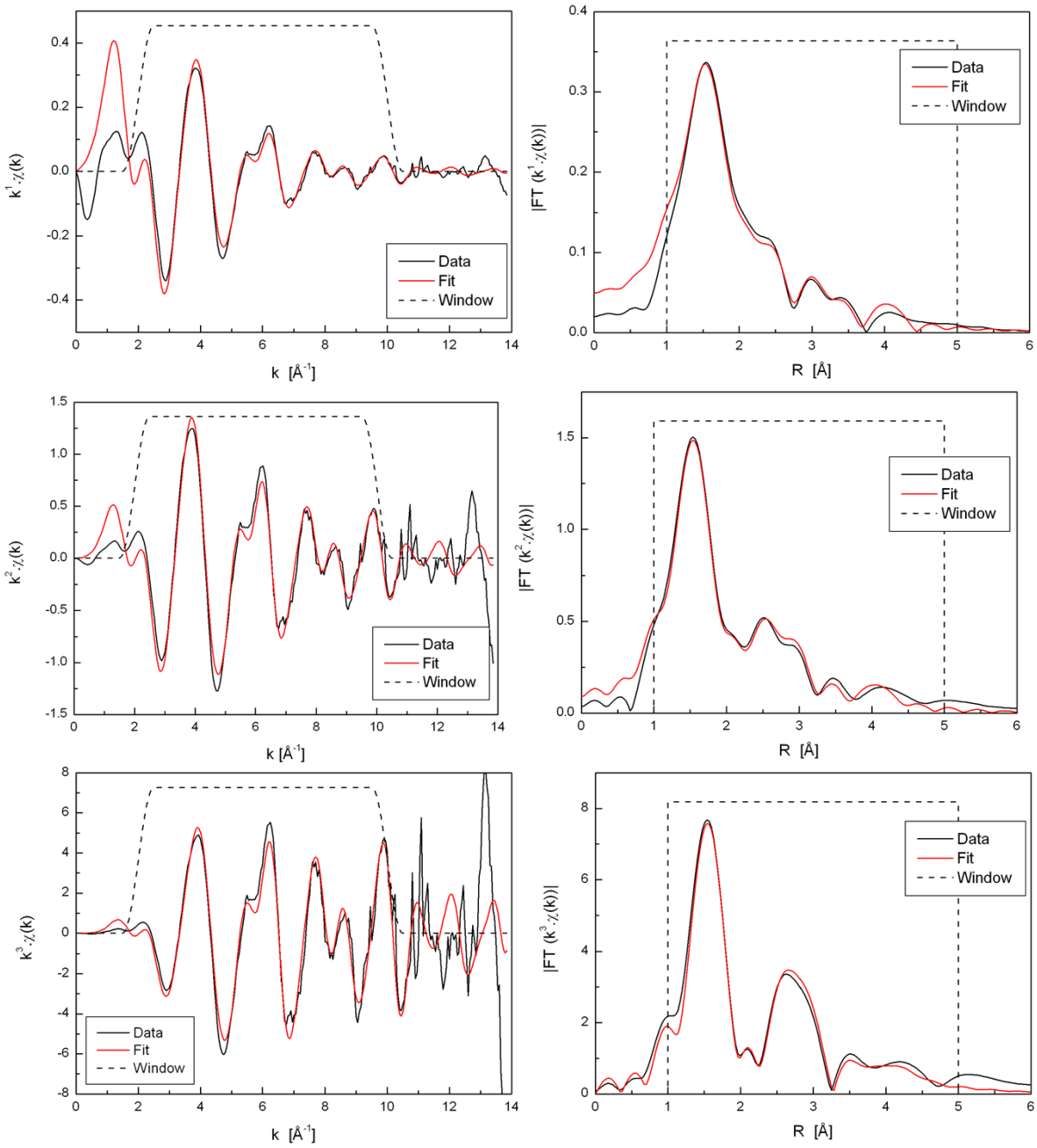

Figure S5. Ni-NCS 2:1 KSCN:Ni^{2+} mole ratio model solution in DMSO ('Sample 5'), fitted using a single shell model. EXAFS data (black lines) and fits (red lines) in k-space (left) and R-space (right) for various k-weightings: k^1 (top), k^2 (middle), k^3 (bottom). The data ranges used for fitting are shown by the window functions (black dashed lines).

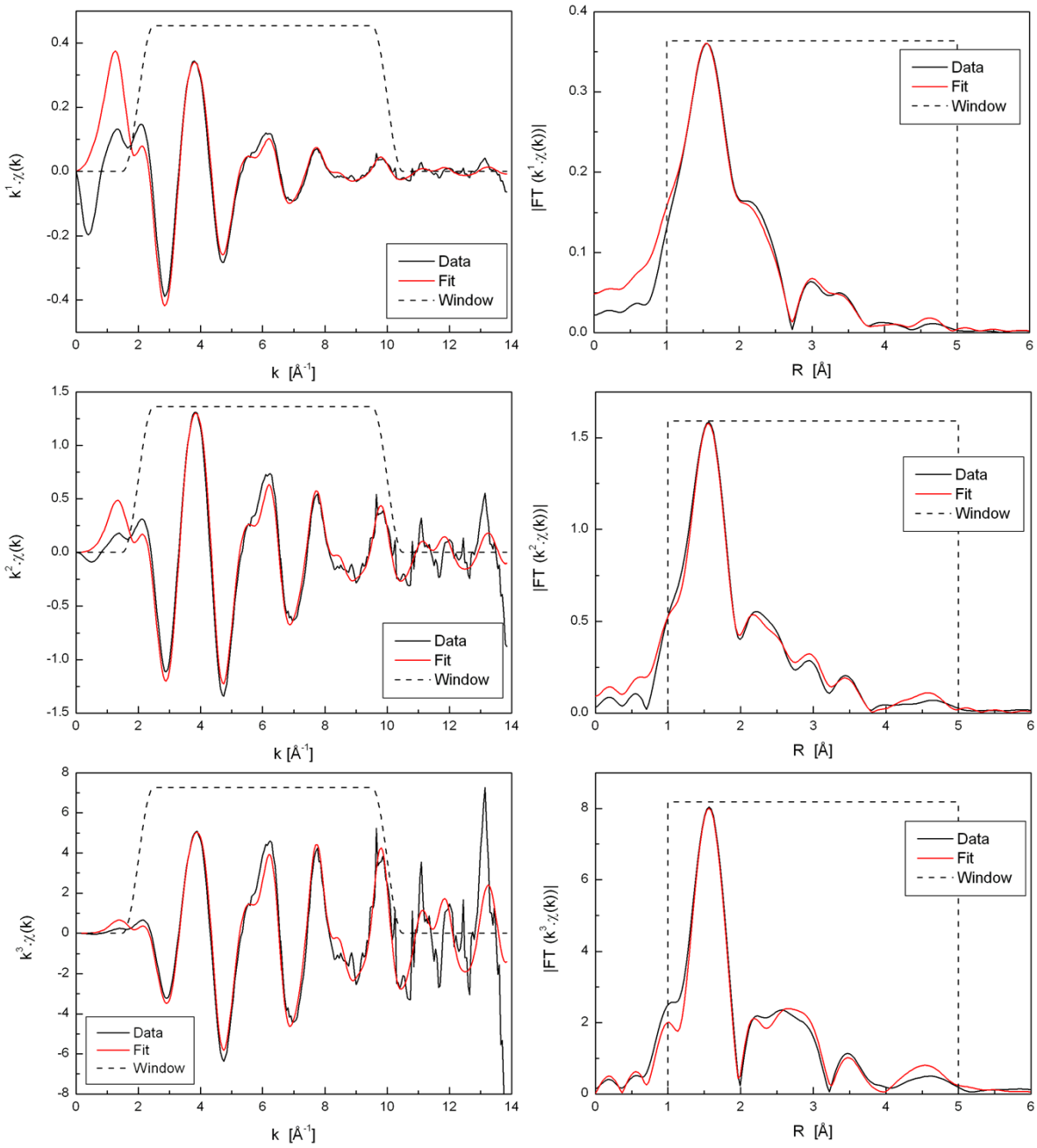

Figure S6. Ni-NCSe 2:1 KSeCN:Ni^{2+} mole ratio model solution in DMSO ('Sample 6'), fitted using a single shell model. EXAFS data (black lines) and fits (red lines) in k-space (left) and R-space (right) for various k-weightings: k^1 (top), k^2 (middle), k^3 (bottom). The data ranges used for fitting are shown by the window functions (black dashed lines).

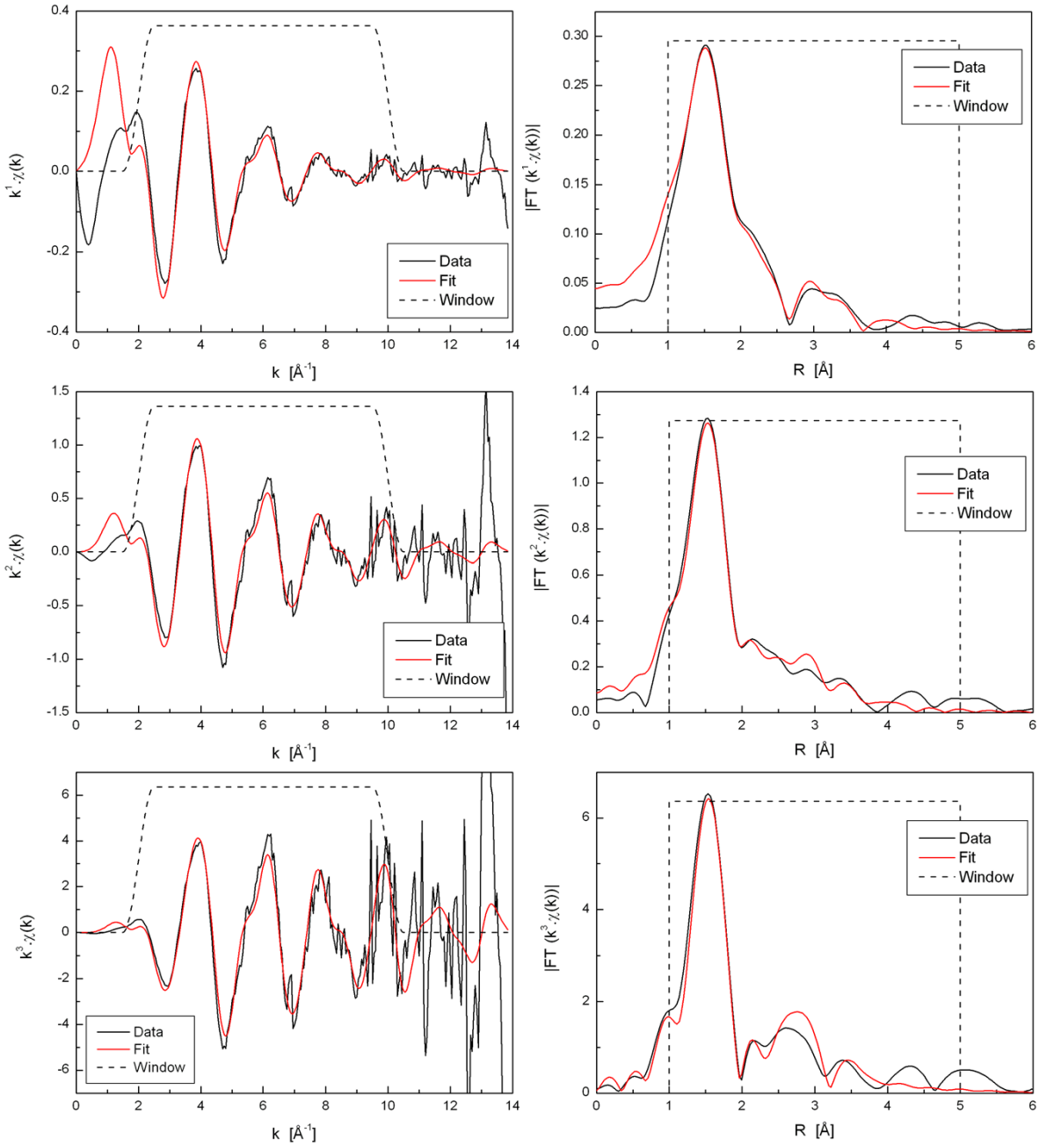

Figure S7. Ni-NCO electrochemically generated solution in DMSO ('Sample 7'), fitted using a single shell model. EXAFS data (black lines) and fits (red lines) in k-space (left) and R-space (right) for various k-weightings: k^1 (top), k^2 (middle), k^3 (bottom). The data ranges used for fitting are shown by the window functions (black dashed lines).

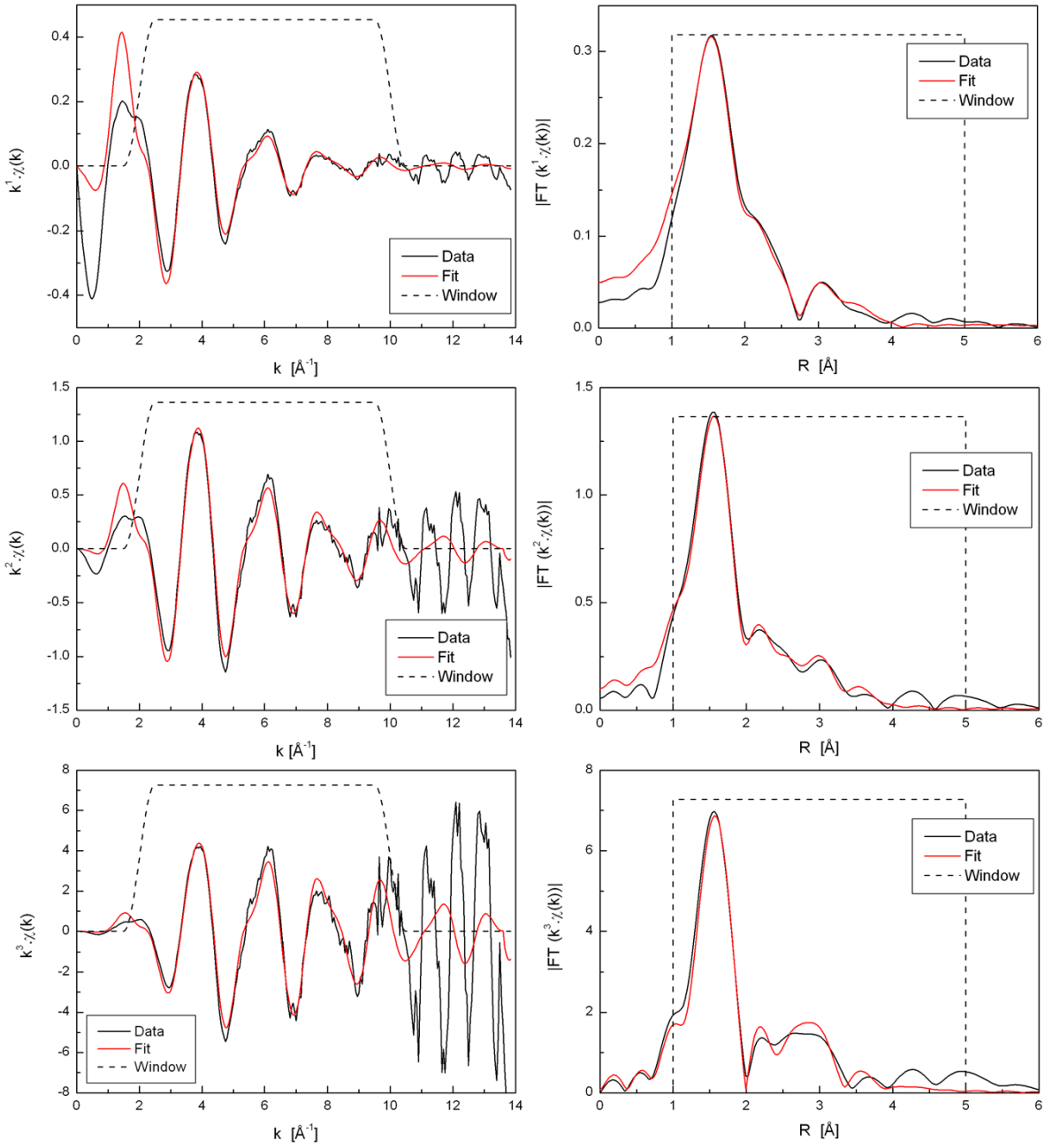

Figure S8. Ni-NCO 2:1 KOCN:Ni^{2+} mole ratio model solution in DMSO ('Sample 4'), fitted using a single shell model for DMSO and a multiple-scattering model for OCN. EXAFS data (black lines) and fits (red lines) in k-space (left) and R-space (right) for various k-weightings: k^1 (top), k^2 (middle), k^3 (bottom). The data ranges used for fitting are shown by the window functions (black dashed lines).

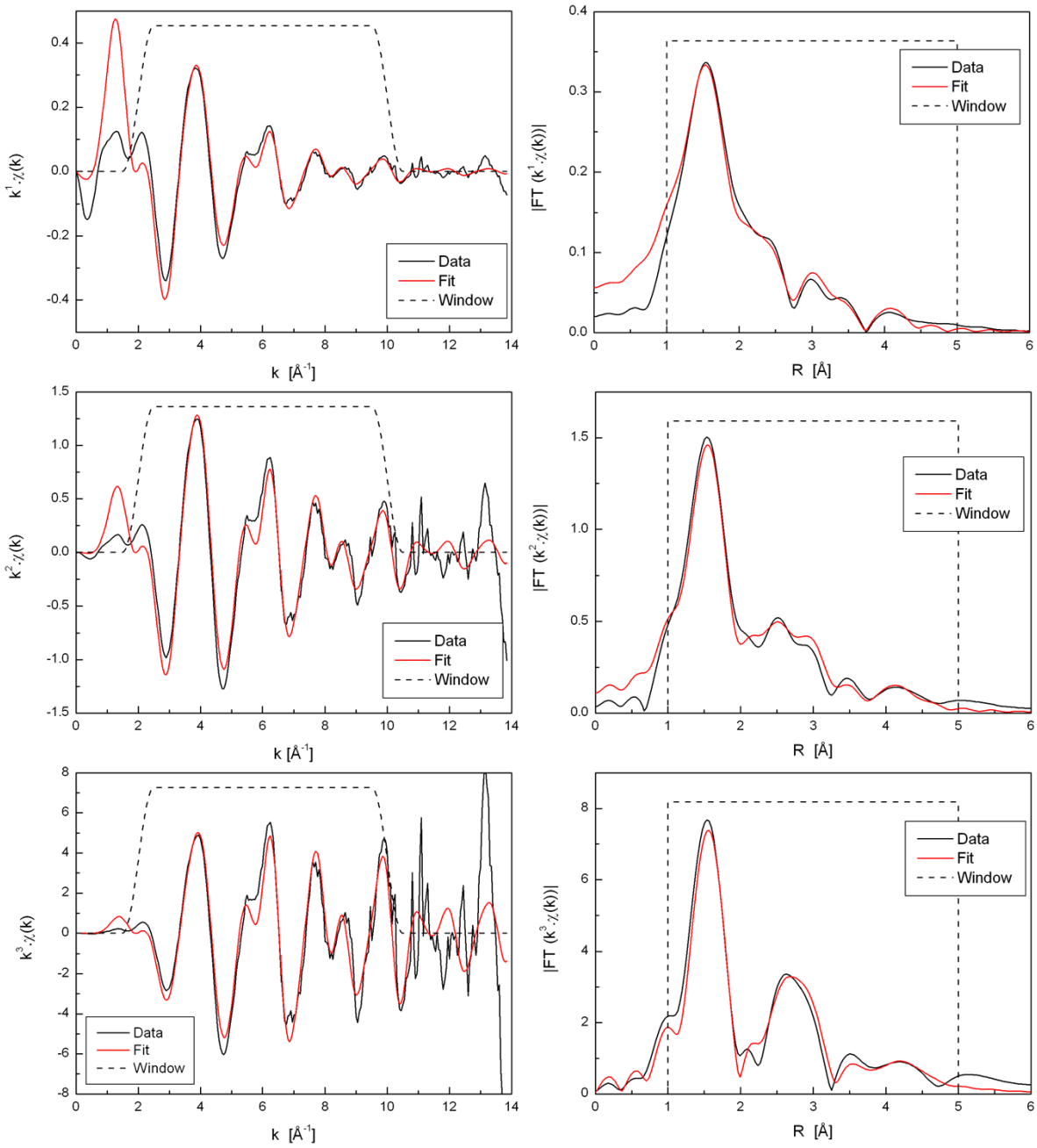

Figure S9. Ni-NCS 2:1 KSCN:Ni^{2+} mole ratio model solution in DMSO ('Sample 5'), fitted using a single shell model for DMSO and a multiple-scattering model for SCN. EXAFS data (black lines) and fits (red lines) in k-space (left) and R-space (right) for various k-weightings: k^1 (top), k^2 (middle), k^3 (bottom). The data ranges used for fitting are shown by the window functions (black dashed lines).

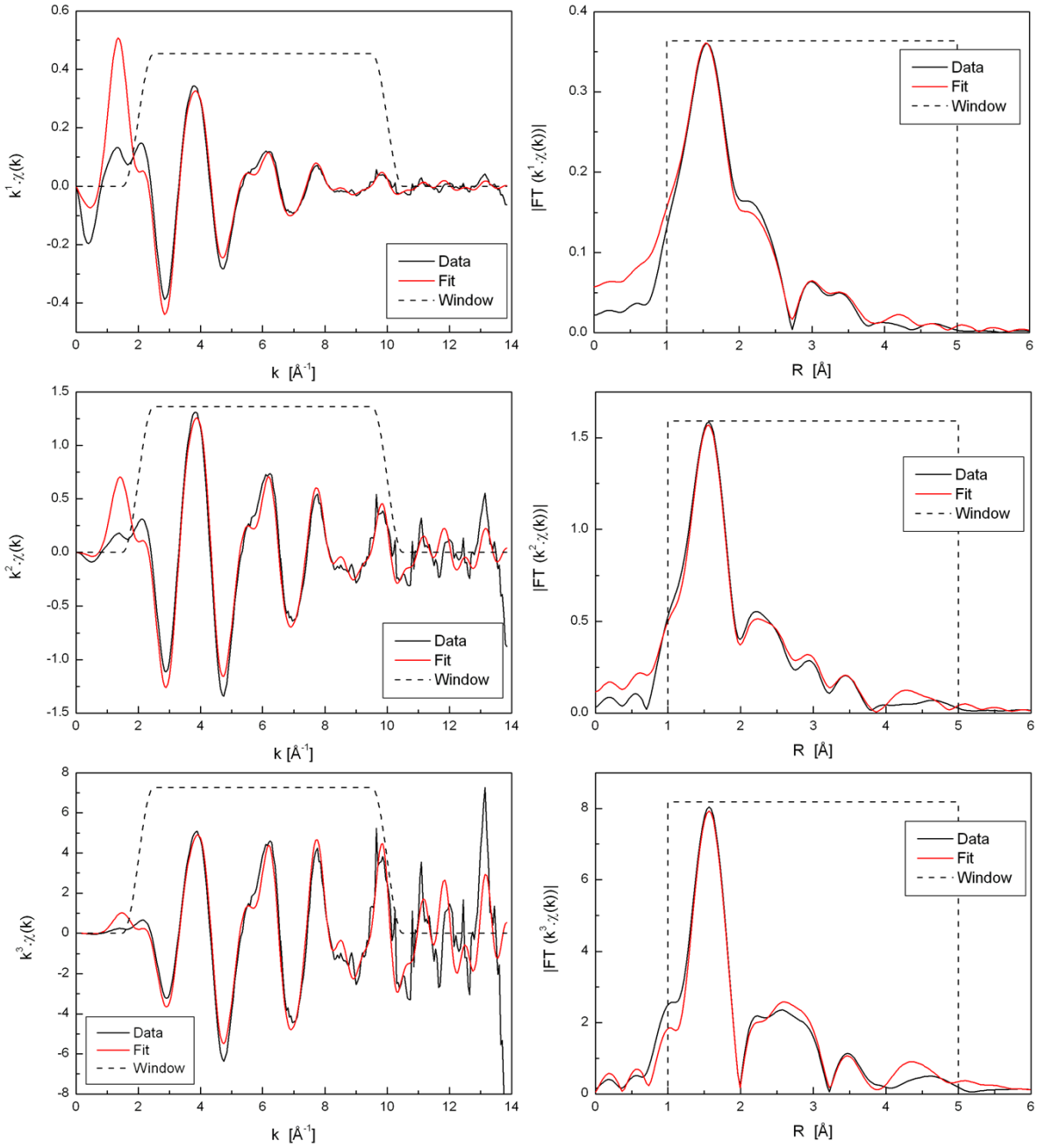

Figure S10. Ni-NCSe 2:1 KSeCN:Ni^{2+} mole ratio model solution in DMSO ('Sample 6'), fitted using a single shell model for DMSO and a multiple-scattering model for SeCN. EXAFS data (black lines) and fits (red lines) in k-space (left) and R-space (right) for various k-weightings: k^1 (top), k^2 (middle), k^3 (bottom). The data ranges used for fitting are shown by the window functions (black dashed lines).

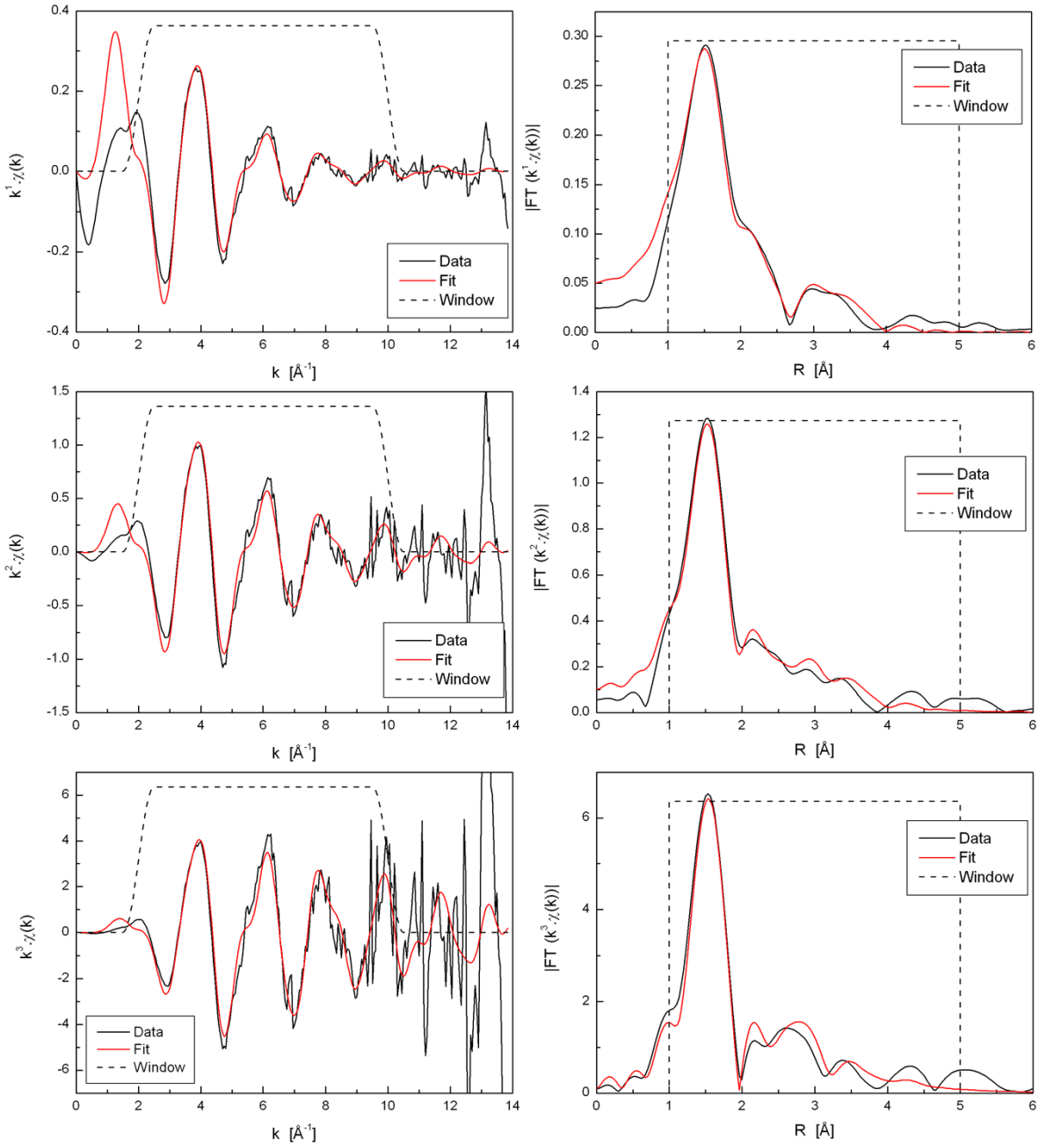

Figure S11. Ni-NCO electrochemically generated solution in DMSO ('Sample 7'), fitted using a single shell model for DMSO and a multiple-scattering model for OCN. EXAFS data (black lines) and fits (red lines) in k-space (left) and R-space (right) for various k-weightings: k^1 (top), k^2 (middle), k^3 (bottom). The data ranges used for fitting are shown by the window functions (black dashed lines).