

Supplementary Information

1) Rietveld analysis of the XRD data was performed using JANA 2006.¹

The atomic coordinates and atomic displacement parameters are reported in Table S1. The reflections observed in the X-ray powder pattern can be indexed in a small unit cell with a axis equal to one-third that of the α -Fe₂WO₆, the low temperature form of Fe₂WO₆ with the columbite structure.² It is as if the structure adopts the α -PbO₂ structure without cation ordering and has a single mixed Fe/W site distributed in the unit cell (Figure S1). Note that the Le Bail refinement in the columbite structure ($3a, b, c$; $Pbcn$ space group) resulted in inferior profile fitting and worst GOF (goodness of fit). Consequently, the model in the small cell (a, b, c ; $Pbcn$ space group) was used to do the Rietveld refinement.

| Atom | Wyck. pos. | x | y | z | SOF | $U_{iso} (\text{\AA}^2)$ |
|------|------------|----------|-----------|----------|--------|--------------------------|
| Fe1 | 4c | 0 | 0.1654(5) | 0.75 | 0.6667 | 0.0206(17) |
| W1 | 4c | 0 | 0.1654(5) | 0.75 | 0.3333 | 0.0206(17) |
| O1 | 8d | 0.233(3) | 0.144(2) | 0.427(2) | 1 | 0.012(4) |

Table S1. Atomic coordinates and atomic displacement parameters of Fe₂WO₆ polyol sample at 800°C with $a = 4.5995(15) \text{ \AA}$, $b = 5.6043(19) \text{ \AA}$, $c = 4.9718(19) \text{ \AA}$, $V = 128.16(8) \text{ \AA}^3$, SG $Pbcn$.

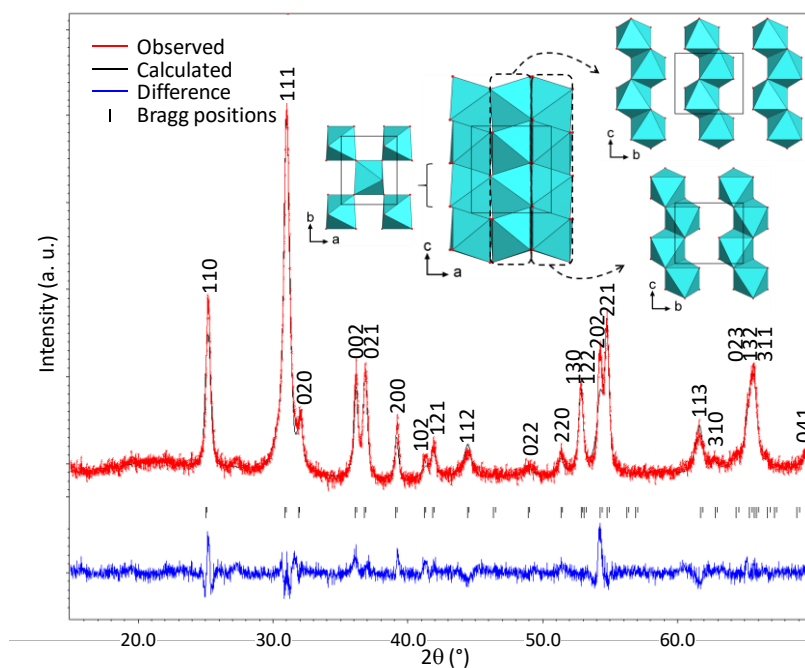


Figure S1. Final Rietveld refinement plot of the XRD data at 800°C of the Fe₂WO₆ polyol sample with Cu-K α 1-K α 2 radiation ($R(\text{obs}) = 3.26 \%$, $\text{GOF} = 1.33$, $wRp = 5.61 \%$). The inset shows the hypothetical structure of Fe₂WO₆ that can be described as the stacking along the a axis of layers made of zigzag chains of edge-sharing Fe/W octahedra shifted from one layer to another with a $(1/2, 1/2, 0)$ vector. Layers are connected to each other through corner sharing octahedra.

2) Mössbauer experiments

^{57}Fe Mössbauer spectra were measured in transmission mode with a $^{57}\text{CoRh}$ source. During the measurements, both the source and the absorber were kept at ambient temperature (294 K). The spectrometer was operated in the constant acceleration mode with a triangular velocity waveform. The velocity scale was calibrated with the magnetically split sextet spectrum of a high-purity $\alpha\text{-Fe}$ reference absorber at room temperature. Since the fitting of the data is not possible using one doublet (one environment), they were fitted with an appropriate distribution of 6 Lorentzian profiles representing quadrupole doublets by least-squares methods using the program PC-Mos II³. In this way, spectral parameters such as the quadrupole splitting (QS), the isomer shift (IS), the linewidth at half maximum (LW) of the different spectral components were determined. Isomer shifts are given relative to the $\alpha\text{-Fe}$.

Mössbauer spectra of the as prepared electrode, after being soaked in the electrolyte (blank) and after 10000 cycles are shown in figure S2, with the 6 Lorentzian profiles necessary, due to the distribution of the different Fe site environments. Figure S3 shows the Quadrupole Splitting distribution of the 6 contributions.

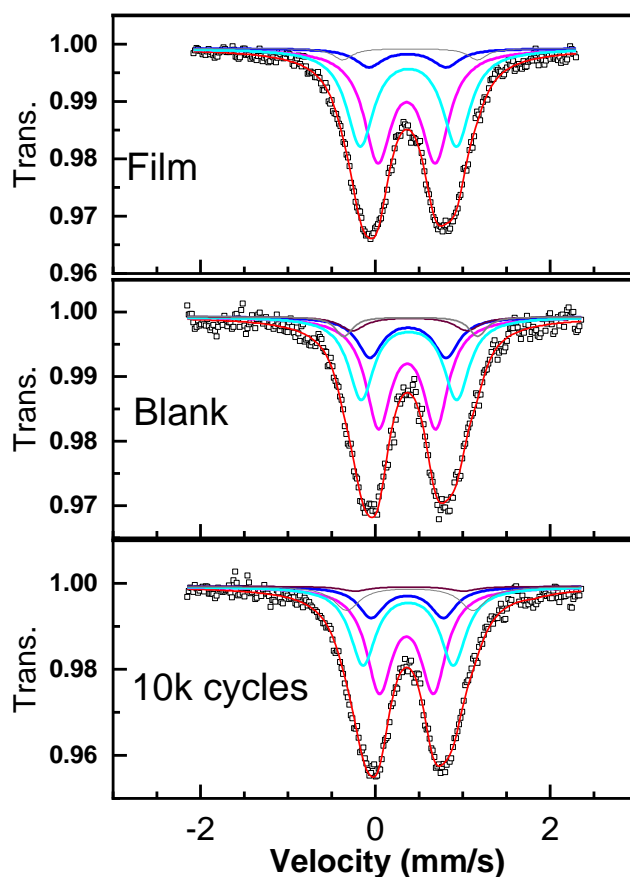


Figure S2. Room temperature ^{57}Fe Mössbauer spectra of all the samples showing the described in the text

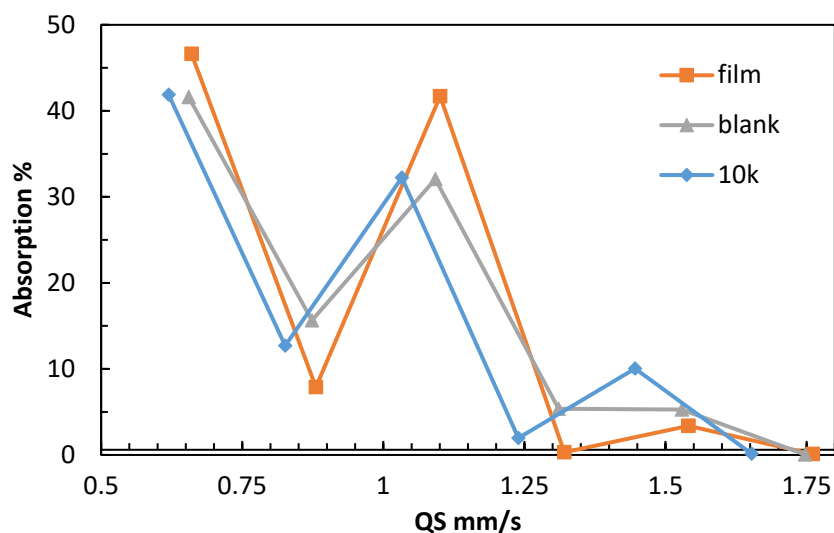


Figure S3. QS distribution for the three samples

Reference

1. Petříček, V.; Dušek, M.; Palatinus, L. Crystallographic Computing System JANA2006: General Features. *Zeitschrift für Kristallographie - Crystalline Materials* **2014**, *229*, 345–352, doi:10.1515/zkri-2014-1737.
2. Guskos, N.; Sadlowski, L.; Typek, J.; Likodimos, V.; Gamari-Seale, H.; Bojanowski, B.; Wabia, M.; Walczak, J.; Rychlowska-Himmel, I. Magnetic and EPR Studies of α -, β -, and γ -Fe₂WO₆ Phases at Low Temperatures. *Journal of Solid State Chemistry* **1995**, *120*, 216–222, doi:10.1006/jssc.1995.1401.
3. Grosse, G. PC-Mos II, Version 1.0 Manual and Program Documentation; 1993 by FASTComTec, Oberhaching, Germany.