Supplementary material to the manuscript

„Charge Attachment Induced Transport – Bulk and Grain Boundary Diffusion of Potassium in PrMnO₃“

By J. Martin et al.

In the main manuscript (section 3.1) we have presented the normalization procedure of the ToF-SIMS raw data, which is shown in Figure S1 below.

![Figure S1: ToF-SIMS raw data of the normalized data shown in Figure 1 (main manuscript).](image)

In the discussion we mentioned that a cesium containing mass fragment (Cs₂O⁺⁺, m/z = 140.9052) interferes with the Pr⁺-signal (m/z = 140.9077). Since we use a ToF-SIMS⁵ (ION TOF GmbH, Münster, Germany) with a mass resolution of about \( m/\Delta m = 8000 \), we are not able to distinguish between the Pr⁺ and Cs₂O⁺⁺-ion signal (\( \Delta m_{\text{max}}(141) = 0.0176 \)). As a consequence we have compared the concentration profiles obtained by cesium and by oxygen sputtering (see Figure S2).

![Figure S2: ToF-SIMS-Analysis of a PMO reference without K⁺-BIIT. The investigated PMO sample and its reference have been synthesized simultaneously. For yielding the concentration profile in (a) we used the Cs⁺-sputter gun and for (b) the O₂⁺-sputter gun was used.](image)
In Figure S2A it is observed, that at the PMO-Pt-interface the Cs$^+$ and the Pr$^+$-ion signal are increasing. As it is not expected, that the praseodymium is accumulated at the PMO-Pt-interface, we assume that this peak in the signal is caused by the Cs$_2$O$^+$ fragment. In Figure S2B there are no cesium ions used for sputtering and the accumulation of praseodymium at the PMO-Pt-interface was not observed. Furthermore the Pr$^+$ and PrO$^+$ trace show a similar behavior.

We have further commented in the main text that the sum of normalized K$^+$ and Pr$^+$ Signals is constant inside the PMO bulk.

To demonstrate this we have normalized K$^+$ trace to the local intensity maximum around 17nm and the Pr$^+$ trace to the local maximum at the interface between the PMO and the Pt electrode around 260nm. These traces are shown in Figure S3.

Figure S3 also shows the sum of these two normalized traces K$^+$ and Pr$^+$. Evidently the sum has a constant value of about 0.9 between 40nm and 240nm. This lends support to the interpretation that the K$^+$ ions indeed enter into the Pr$^+$ sites and consequently replace the latter.