Supplementary material to the manuscript

"Charge Attachment Induced Transport – Bulk and Grain Boundary Diffusion of Potassium in $\text{PrMnO}_3\text{``}$

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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).

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/ Δ m = 8000, we are not able to distinguish between the Pr⁺ and Cs₂O⁺⁺-ion signal ($\Delta m_{max}(141) = 0.0176$). 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 O_2^+ -sputter gun was used.

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 Cs₂O⁺ 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: Illustration of the correlation between K⁺ and Pr⁺ signals. K⁺ and Pr⁺ traces have been normalized at 17nm and 260nm respectively. Also shown is the sum of the normalized traces K⁺ and Pr⁺ as well as a line at intensity 1 to guide the eye.

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 indead enter into the Pr^+ sites and consequently replace the latter.