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2θ(Cu *Kα*)/°

Figure 1S High temperature XRD of $Ba_3(MnO_4)_{2.}$



Figure 2S Surface SEM images of (a) $Ba_3(MnO_4)_2$, (b) $Ba_3(MnO_4)_2$ -ATO, (c) LSCF anodes, and (d) cross-section SEM images of $BaZr_{0.4}Ce_{0.4}Y_{0.2}O_3$ sintered disc.



Figure 3S XRD patterns of commercial ATO and

Figure 3S XRD patterns of commercial ATO and $Ba_3(MnO_4)_2$ -ATO mixed electrodes before and after electrolysis at 2.0 V for 3h at 700° C.