

Supporting Information

Low Temperature Performance of a Ferroelectric Glass Electrolyte Rechargeable Cell

M.H. Braga^{1*}, A.J. Murchison², J.E. Oliveira¹, J.B. Goodenough^{2*}

¹LAETA, Engineering Physics Department, Engineering Faculty, University of Porto, R. Dr. Roberto Frias
s/n, 4200-465 Porto, Portugal

²Texas Materials Institute and the Materials Science and Engineering Program, The University of Texas at
Austin, Austin TX 78712 USA

*corresponding authors: mbraga@fe.up.pt and jgoodenough@mail.utexas.edu

Cathode Characterization

The γ -MnO₂ was identified and characterized with X-ray diffraction and SEM/EDS analysis. An X-ray diffraction pattern characteristic of γ -MnO₂ is shown in figure S1. An overlay of the as purchased γ -MnO₂ and the γ -MnO₂ after it had been sintered at 400°C for 24 hours prior to being used in electrochemical measurements were compared with previously published data of γ -MnO₂ [S1]. Figure S3 shows a characteristic morphology of the γ -MnO₂ after sintering that was used for cathode preparation in the full cells measured. Figure S2 shows a line EDS scan and quantitative results showing the atomic percentage of approximately 2:1 for O:Mn. Figure S3 presents EDS mapping and shows a uniform distribution of manganese and oxygen in the material.

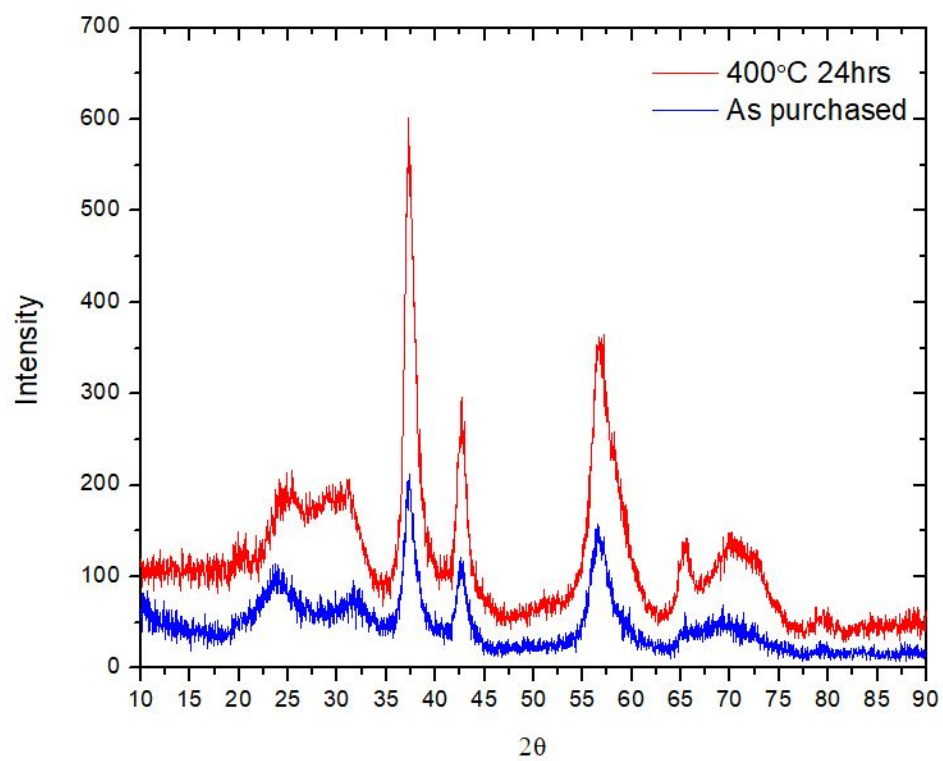


Figure S1 X-Ray Diffraction pattern of γ -MnO₂ active material prior to and after sintering at 400°C for 24 hours

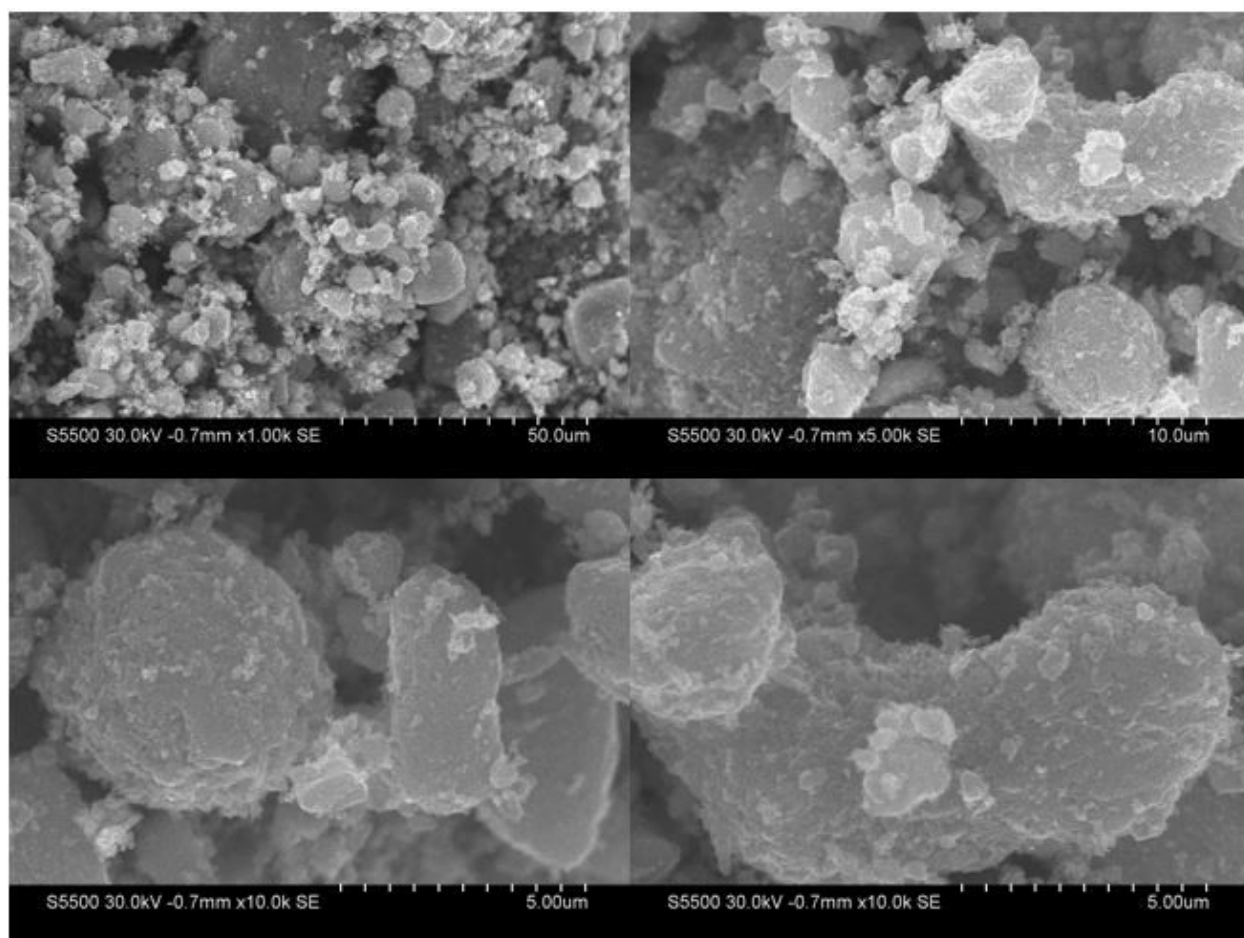
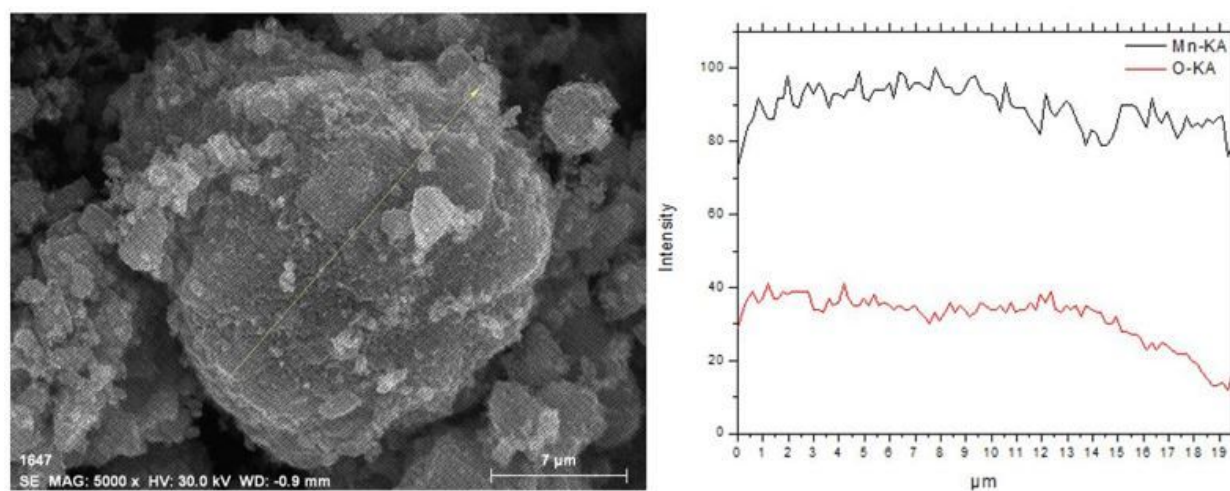


Figure S2 Scanning Electron Microscopy images showing the characteristic morphology of γ -MnO₂ active material after sintering at 400°C for 24 hours



Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]
Oxygen	8	K-series	2033	33.66732	37.24152	66.34488
Sodium	11	K-series	94	1.37325	1.519037	1.883291
Manganese	25	K-series	9951	55.36209	61.23945	31.77183
Sum:				90.40266	100	100

Figure S3 Energy Dispersive X-Ray line scan results of γ - MnO_2 active material particle after sintering at 400°C for 24 hours showing approximately a 2:1 Oxygen to Mn atomic percentage ratio with trace impurities of sodium.

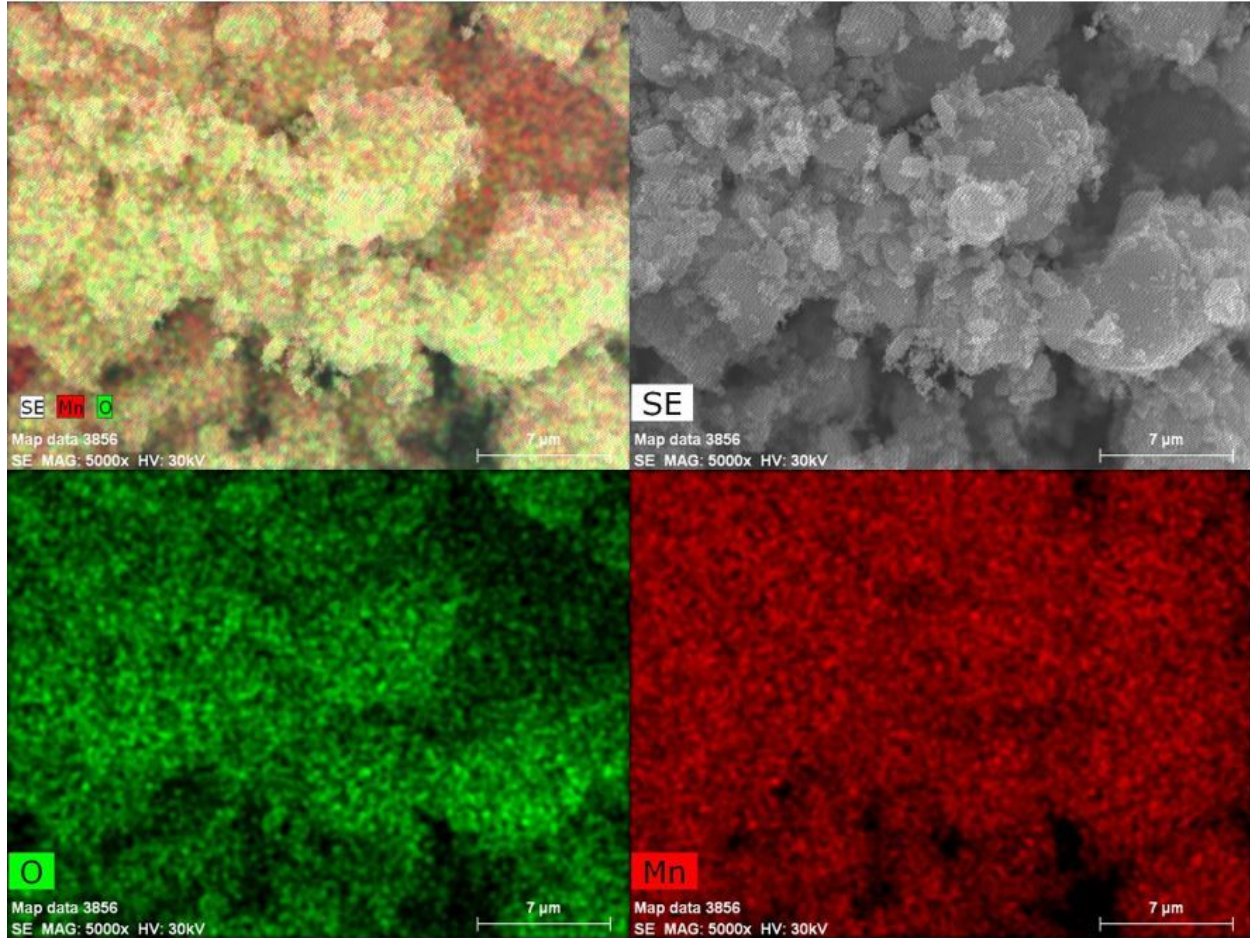


Figure S4 Energy Dispersive X-Ray mapping of γ - MnO_2 active material after sintering at 400°C for 24 hours

Activation Energy Calculations

Activation energy of ionic conduction in the lithium glass electrolyte was calculated using the slopes of the Arrhenius plot shown in Fig. 4c with the relationship

$$\ln(\sigma_{Li}T) = -\frac{\Delta E_a}{1000 k_B} \frac{1000}{T}$$

Where $-\frac{\Delta E_a}{1000 k_B}$ is the slope of the Arrhenius plot, ΔE_a motional enthalpy or activation energy of the ionic conduction process, and k_B is the Boltzmann constant.

Current and voltage profiles for a commercial Li-MnO₂ CR1616 coin-cell discharged with a green LED and the comparison with a Li-MnO₂ pouch cell reported here

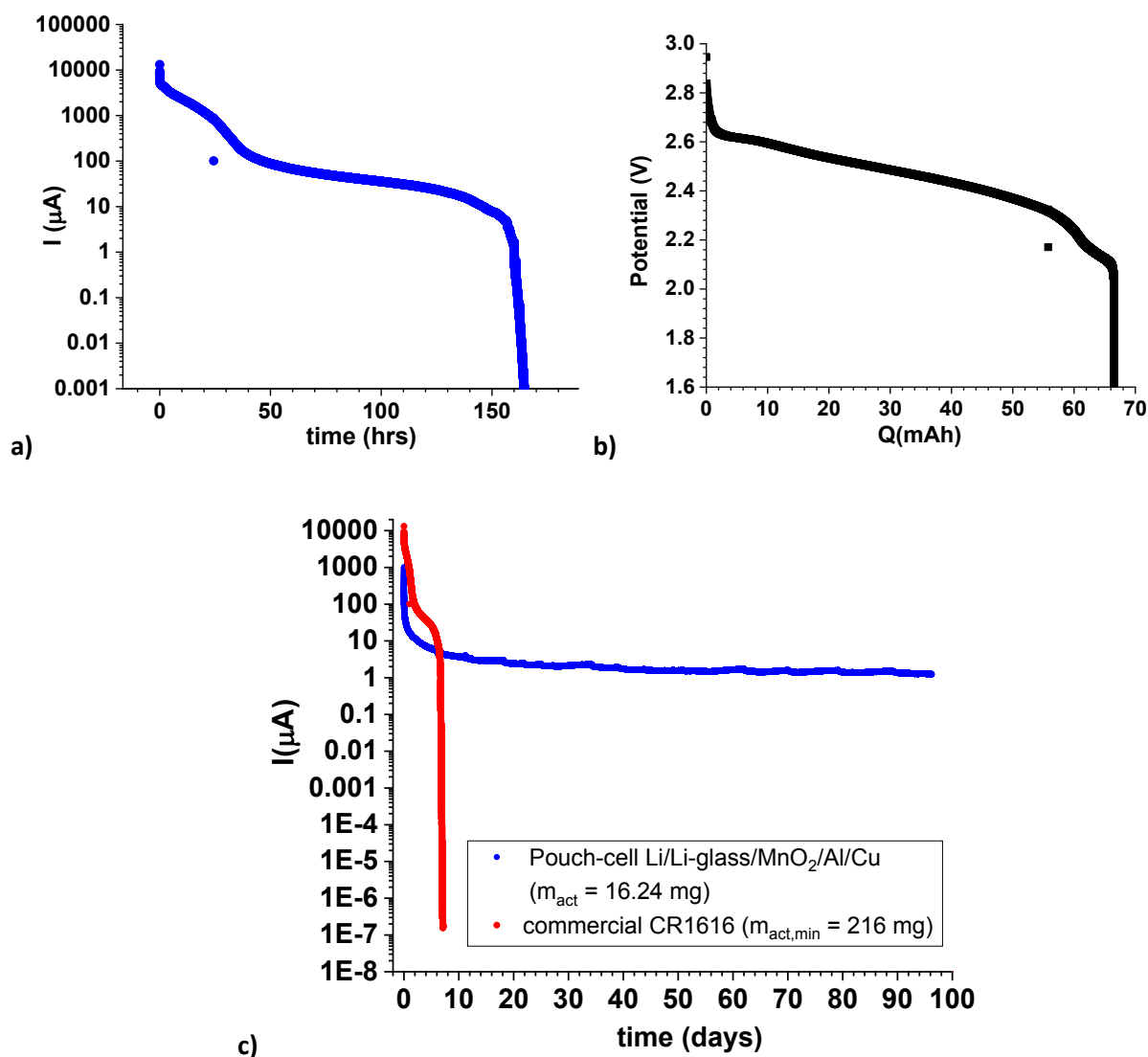


Figure S5 Current and Potential profiles for a commercial Li-MnO₂ CR1616 coin-cell (liquid electrolyte) discharged with a green LED; **a)** the current profile; **b)** the potential profile; **c)** comparison between the current profile of the commercial Li-MnO₂ CR1616 coin-cell and Li/Li-glass/ γ -MnO₂/Al pouch-cell with 16.2 mg of active material.

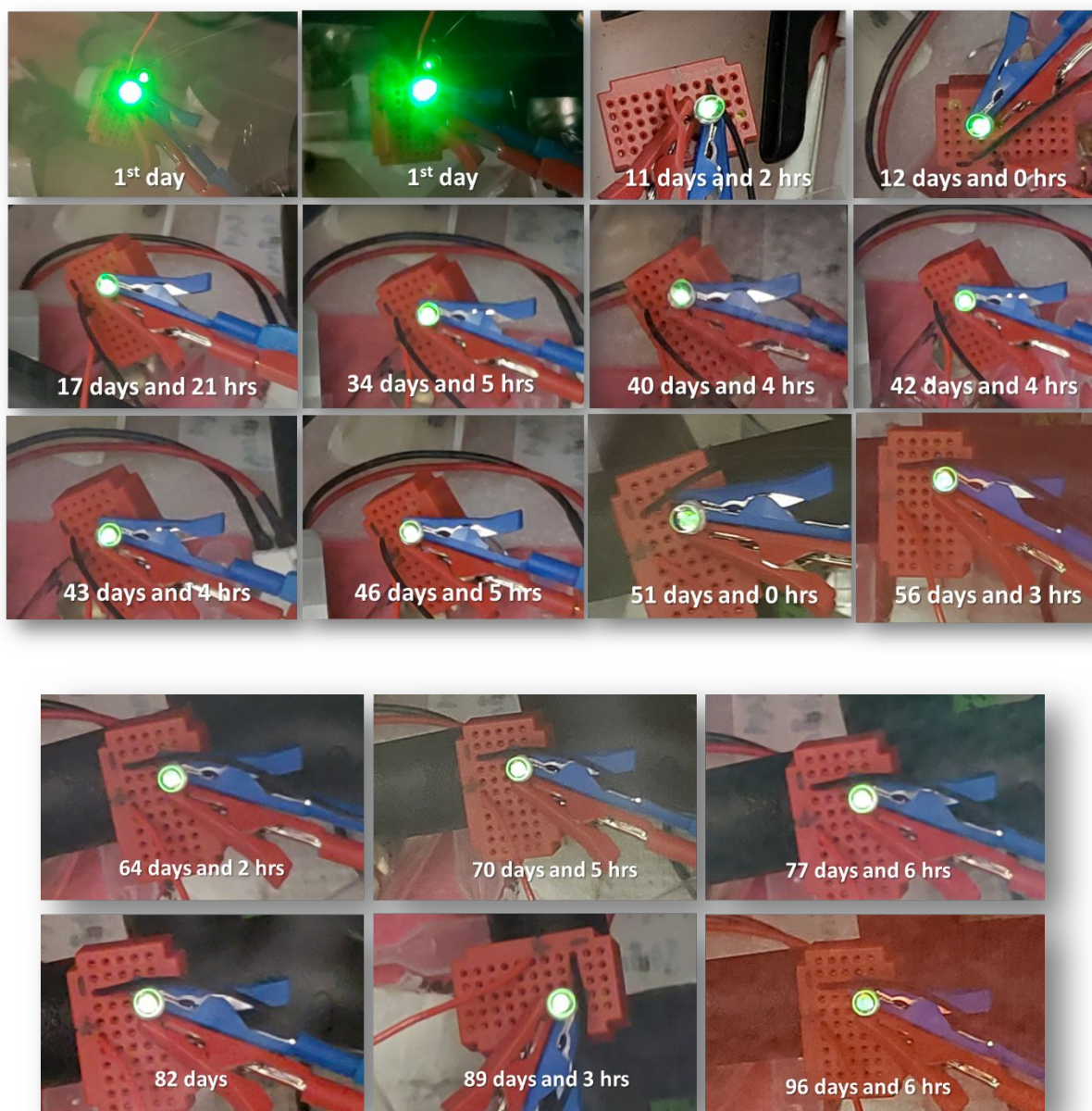


Figure S6 Green LED lit for 96 days and 6 hrs in an Argon filed glove box with a Li/Li-glass/ γ -MnO₂/Al pouch-cell with 16.2 mg of active material.

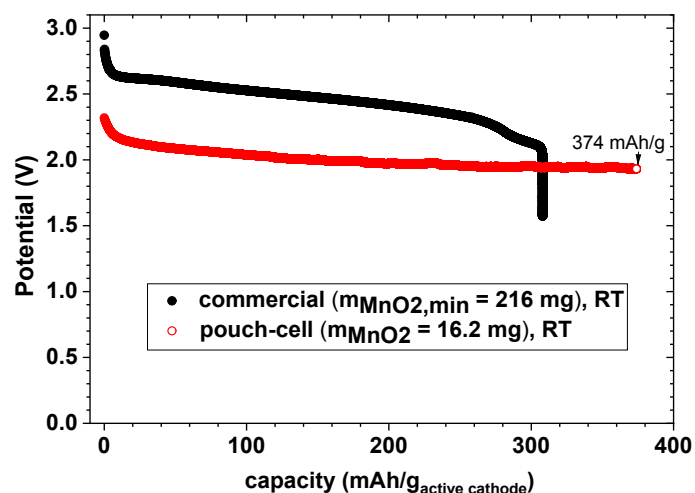


Figure S7 Potential profiles for a commercial Li-MnO₂ CR1616 coin-cell (with liquid electrolyte) and a Li/Li-glass/γ-MnO₂/Al pouch-cell with 16.2 mg of active material both discharged with a green LED. The capacity of the commercial cell was considered to be the theoretical capacity 308 mAh.g⁻¹ (LiMnO₂). The γ-MnO₂ of the pouch cell is smaller than 209 mAh.g⁻¹ (Li₅Mn₇O₁₆).

References

- S1. Alfuruqi, M; Mathew, V; Gim, J; Kim, S; Song, J; Baboo, J; Choi, S; Kim, J “Electrochemically Induced Structural Transformation in a γ-MnO₂ Cathode of a High Capacity Zinc-Ion Battery System”, Chemistry of Materials, 2015, 27 (10), 3609-3620