Supporting online Materials for

# Single Crystalline Thallium Rhodium Oxide Pyrochlore for Highly Improved Round Trip Efficiency of Hybrid Na-air Battery

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## Characterization methods

X-ray diffraction (XRD) patterns were collected (New D8-Advance/Bruker-AXS) at a scan rate of 1° $s^{-1}$ within the 2θ range of 10°–80° using Cu $K_{\alpha1}$ radiation (0.154056 nm). The morphologies of the samples were analyzed using high-resolution transmission electron microscopy (HR-TEM, JEM-3010) and Field emission scanning electron microscopy (FE-SEM, SIGMA, Carl Zeiss). The X-ray adsorption near edge structure (XANES) were collected on BL10C beam line at the Pohang light source (PLS-II) with top-up mode operation under a ring current of 200 mA at 3.0 GeV. The incident beam was collimated by a Ru-coated mirror at 2.8 mrad and monochromatized using a channel-cut Si (1 1 1) monochromator. The beamline energy was calibrated with Pt reference foil to the Pt $L_{III}$-edge position at 11564 eV. Ionization chambers filled with $N_2$-Ar was gas mixtures were used for XAS detection in transmission mode, where a Pt reference foil was measured congruently with the sample between the second and third ionization chambers.

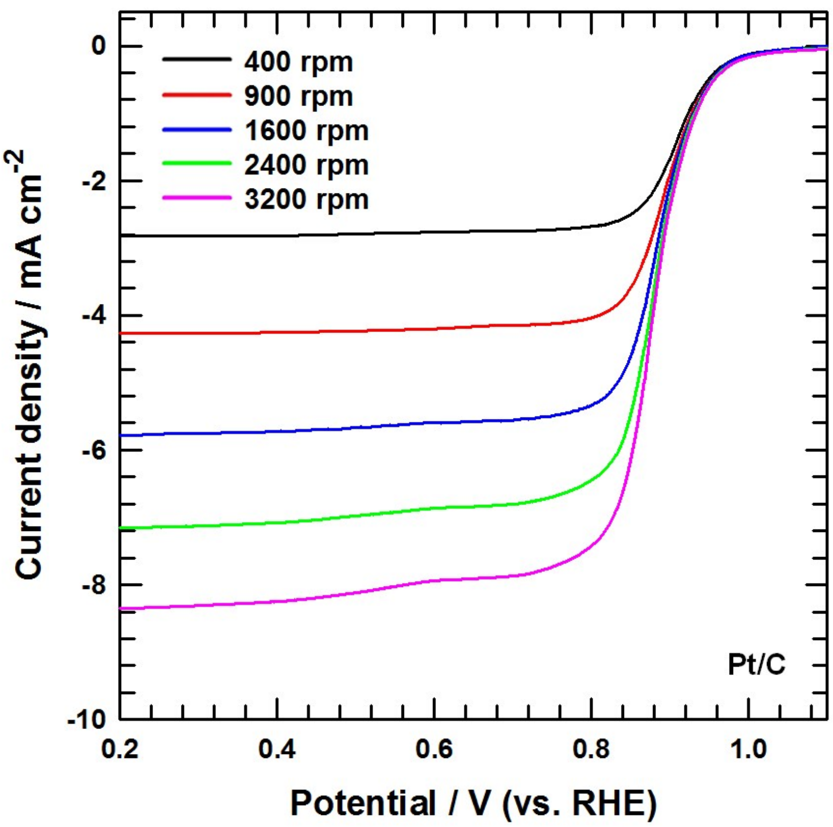


**Figure S1.** ORR LSV curves for Pt/C at different rotating speeds with a scan rate of 10 mV $s^{-1}$.

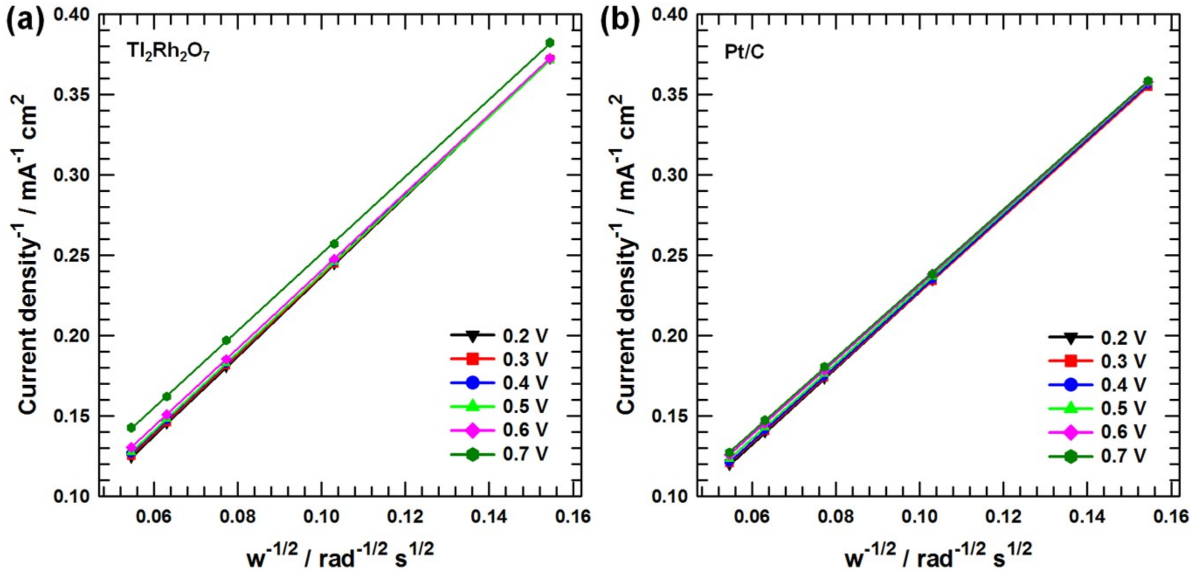


**Figure S2.** (a) Koutecky-Levich plots derived from the ORR LSV curves of $Tl_2Rh_2O_7$. (b) Koutecky-Levich plots derived from the ORR LSV curves of Pt/C. The rpm is converted to radian $sec^{-1}$ by using following equation : $rad\ s^{-1} = \frac{rpm\ \times 2\ \times \pi}{60}$

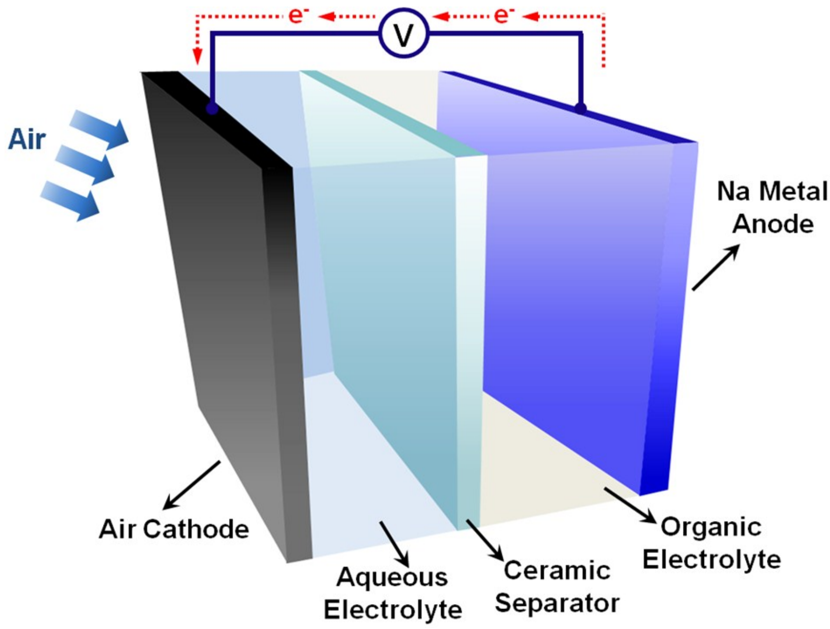


**Figure S3.** Schematic representation of the preparation of hybrid Na-air battery.

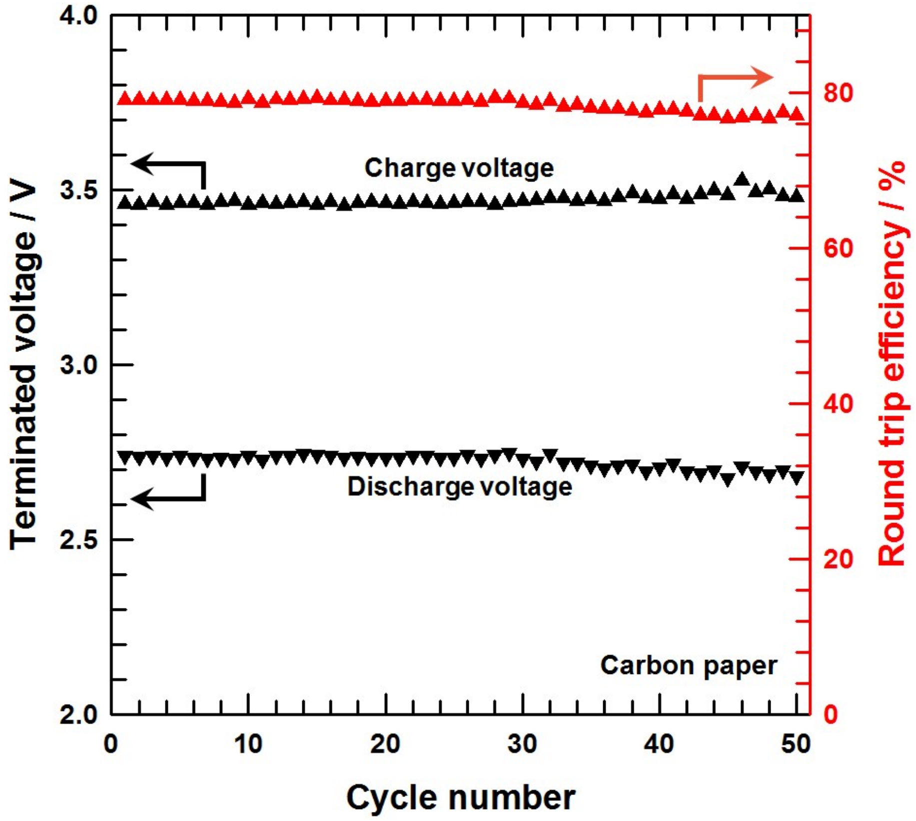


**Figure S4.** Cycling stability of bare carbon paper electrode up to 50 cycles with terminated charge and discharge voltage and round trip efficiency.

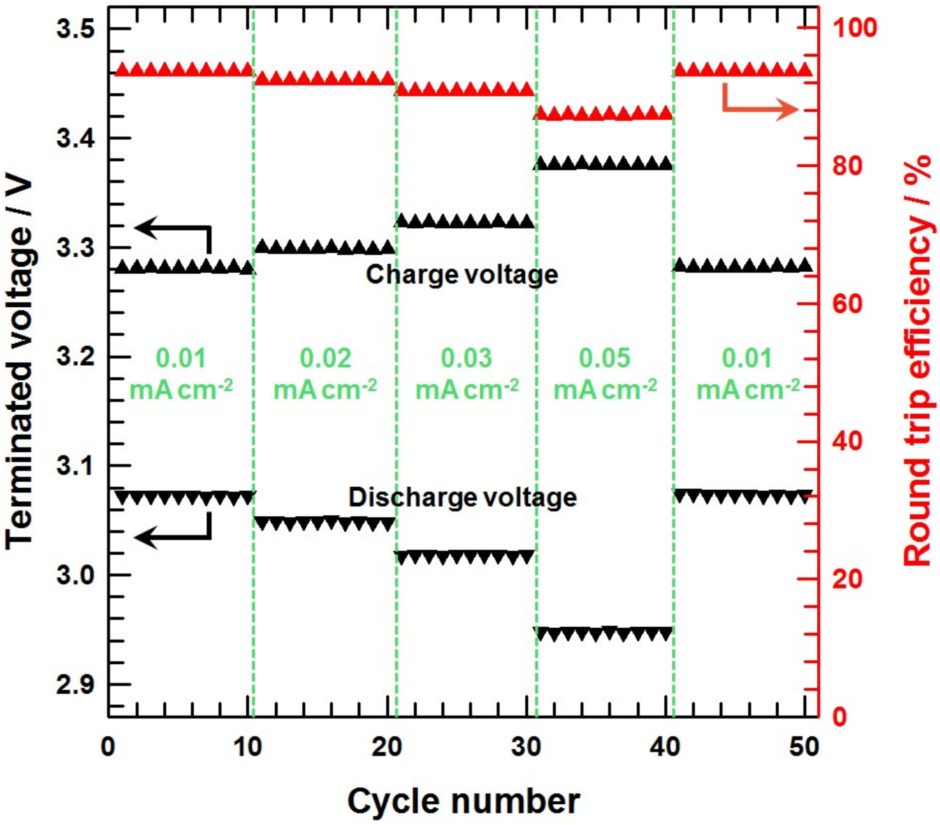


**Figure S5.** Cycling terminated charge and discharge voltage and round trip efficiency profile of $Tl_2Rh_2O_7$ at different current densities.

**Table S1.** Comparison of the ORR activity of $Tl_2Rh_2O_7$ with other electrocatalysts previously reported.

| Catalyst | Electrolyte | $E_{ORR}$ [at -3 mA cm$^{-2}$] | Ref |
|---|---|---|---|
| Mn oxide | 0.1 M KOH | 0.73V | 1 |
| PCN-CFP | 0.1 M KOH | 0.67V | 2 |
| $Ni_3Fe$/N-C sheets | 0.1 M KOH | 0.78V | 3 |
| $NiCo_2O_4$/G | 0.1 M KOH | 0.56V | 4 |
| N, S-CN | 0.1 M KOH | 0.77V | 5 |
| $Co_3O_4$/2.7$Co_2MnO_4$ | 0.1 M KOH | 0.68V | 6 |
| Co/N-C-800 | 0.1 M KOH | 0.74V | 7 |
| $NiCo_2S_4$@N/S-rGO | 0.1 M KOH | 0.72V | 8 |
| $Tl_2Rh_2O_7$ | 0.1 M KOH | 0.832V | This work |

**Table S2.** Comparison of oxygen electrode activity of $Tl_2Rh_2O_7$ with other electrocatalysts previously reported, including metal oxide based, perovskite based carbon based, pyrochole oxide based bifunctional electrocatalysts.

| Catalyst | | $E_{OER, at 10 mA cm-2}$ - $E_{ORR, at -3 mA cm-2}$ | Ref |
|---|---|---|---|
| Metal oxide-based | CoO/N-Graphene | 0.76V | 9 |
| | $MnO_x$ Film | 1.06V | 10 |
| | $MnCoO_x$/N-Carbon | 0.84V | 11 |
| | $Co_3O_4$/N-Graphene | 0.71V | 12 |
| | $Co_3O_4$-Carbon | 0.74V | 13 |
| | $NiCo_2O_4$/Graphene | 0.96V | 4 |
| | $Mn_xO_y$/N-Carbon | 0.87V | 14 |
| | LT-$Li_{0.5}CoO_2$ | 1.00V | 15 |
| | $Co_3O_4$/N,S-Carbon | 0.79V | 16 |
| Perovskite-based | La(BaSr)CoFeO | 1.01V | 17 |
| | $LaNiO_{3-\delta}$ | 1.04V | 18 |
| | ns$LANiO_3$/N-Carbon | 0.97V | 19 |
| | $LaNiO_3$/N-CNT | 0.95V | 20 |
| Carbon-based | N-Graphene/CNT | 0.95V | 21 |
| | N-Carbon | 0.84V | 22 |
| | Fe, N-Carbon | 0.76V | 23 |
| | N-CNT/Graphene | 0.91V | 24 |
| | P, N-Carbon Fiber | 0.96V | 2 |
| | GNS/MC | 0.72V | 25 |
| | Fe-Mc | 0.88V | 25 |

| | | | |
|---|---|---|---|
| | N, S, Fe-Carbon | 0.91V | 26 |
| Pyrochlore oxide-based | $Pb_2Ru_2O_{6.5}$ | 0.82V | 27 |
| | $Y_2[Ru_{2-x}Y_x]O_{7-y}$ | 1.03V | 28 |
| | $Tl_2Rh_2O_7$ | 0.82V | This work |

**Table S3.** Comparison of electrochemical performance of $Tl_2Rh_2O_7$ with other air electrodes previously reported

| Na-air battery | Current density | Round trip Efficiency | Cycles | Power density | Ref |
|---|---|---|---|---|---|
| Graphitic nanoshell/mesoporous carbon // Aqueous | N/A | 96.2% | 10 | 78.2 mW $g^{-1}$ at 60 mA $g^{-1}$ | 25 |
| Carbon black on Al mesh // Non-Aqueous | 200 mA $g^{-1}$ | 47% | 20 | N/A | 29 |
| Mesoporous carbons // Non-Aqueous | 100 mA $g^{-1}$ | 42% | 20 | N/A | 30 |
| VGC // Aqueous | 4 mA $g^{-1}$ | 81% | 50 | 104 mW $g^{-1}$ at 80 mA $g^{-1}$ | 31 |
| CNT/Ni with NaI // Non-aqueous | 0.05 mA $cm^{-2}$ | 55% | 150 | N/A | 32 |
| Porous $CaMnO_3$/C // Non-Aqueous | 100 mA $g^{-1}$ | 55% | 80 | N/A | 33 |
| $MnO_2$/rGO/carbon paper // Aqueous | 15 mA $g^{-1}$ | 81% | 20 | N/A | 34 |
| N-CNT // Non-Aqueous | 75 mA $g^{-1}$ | 53% | 50 | N/A | 35 |
| Pt/C // Aqueous | 0.025 mA $g^{-1}$ | 84.3% | 18 | N/A | 36 |
| N-doped graphene nanosheet // Non-Aqueous | 75 mA $g^{-1}$ | 61% | 03 | N/A | 37 |
| Pt@graphene nanosheets // Non-Aqueous | 0.1 mA $cm^{-2}$ | 68% | 10 | N/A | 38 |
| $Co_3(PO_4)_2$ // Aqueous | 0.05 mA $cm^{-2}$ | 83% | 50 | N/A | 39 |
| $Tl_2Rh_2O_7$ | 0.01 mA $cm^{-2}$ | 93.65% | 50 | 159.9 mW $g^{-1}$ at 120 mA $g^{-1}$ | This work |

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