Electronic Supplementary Information:

Aluminum-Air Battery Based on Ionic Liquid Electrolyte

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1. Electrochemical cell

- **Figure 1.** The electrochemical cells applied for the presented studies
2. XPS Studies

Surface analysis of the air electrode was conducted by XPS (Thermo VG Scientific, Sigma probe, GB) having a base pressure of \(<10^{-9}\) Torr and fitted with a mono-chromatized Al KR (1486.6 eV) X-ray source. The detailed spectra of Al 2p were measured with the pass-energy of 20 eV and step size of 0.05 eV. Spectra were acquired and processed by the XPS Peak Fit software and referenced to the C 1s peak at 285.0 eV. Peak area intensity data were obtained after Shirley type background subtraction. Peak decomposition of the complex lines was performed by peak synthesis method, using mixed Gaussian–Lorenzian peak shape, while minimizing the error between the actual data and the sum of the deconvoluted peaks. Peak fitting solutions were sought for \(\chi^2<1\), where \(\chi^2\) is the standard deviation.

3. Aluminum termination

(a) \(t=0\)

(b) \(t>0\)

![Native Al oxide](native Al oxide)

![AlF_x formation](AlF_x formation)

**Figure. 2S.** Schematic representation of the termination process: (a) Native Al oxide presented in the initial exposure of the surface to the electrolyte, (b) oxide dissolution and AlF_x formation on the Al surface.
4. **Al capacity calculation**

4.1. **Aluminum electrode theoretical capacity**

The Al theoretical capacity was calculated as follow:

\[
\text{Al}_{\text{weight}} = \text{Al}_{\text{volume}} \times \text{Al}_{\text{density}} = 1.13 \text{cm}^2 \times 0.025 \text{cm} \times 2.7 \text{gr/cm}^3 = 0.0762 \text{gr.}
\]

Applying Faraday’s law for theoretical capacity \((Q)\) of the Al electrode is given by:

\[
Q = \frac{nFM}{M_w} = \frac{3e^- \cdot 0.0762[\text{gr}] \cdot 96485[\frac{\text{C}}{\text{mol} \cdot e^-}]}{27[\text{gr/mol}]} = 816.91[\text{C}] = 226.9[\text{mAh}]
\]

Where: \(F\)-Faraday constant, \(n\)-number of electrons passing in the reaction, \(m\)-material weight, \(Q\)-charge passing in the reaction, \(M_w\)-material molecular weight

4.2. **Al practical energy per weight unit**

Al electrode practical energy per weight unit is varying with the applied discharge currents. For example, for cell discharge current density of 1.5mA/cm²:

\[
E(\text{energy per weight unit}) = \frac{V_{\text{dvp}} \cdot q}{m} = \frac{1.1[V] \cdot 160 \cdot 10^{-3}[\text{Ah}]}{0.0762 \cdot 10^{-3}[\text{Kg}]} = 2,315[\text{Wh/Kg}]
\]

Where \(V_{\text{dvp}}\)-discharge voltage plateau, \(q\)-charge passing in the reaction, \(m\)-material weight

4.3. **Cell practical energy per weight unit and per volume unit**

Cell (including all active materials) practical energy per weight unit is varying with the applied discharge currents that expected for coin cell shown in Figure. 3S.

![Cell components](image)

**Figure. 3S.** Schematic illustration of the cell components.
For example, for cell discharge current density of 1.5mA/cm$^2$:

$$E(\text{energy per weight unit}) = \frac{V_{dvp} \cdot q}{m_A + m_{SS} + m_C} = \frac{1.1[V] \cdot 160 \cdot 10^{-3}[Ah]}{(0.0762 + 0.065 + 0.049) \cdot 10^{-3}[kg]} = 925[Wh/kg]$$

Where $V_{dvp}$ is discharge voltage plateau, $q$ is charge passing in the reaction, $m_A$ is anode weight, $m_{SS}$ is anode weight soaked with electrolyte separator weight, and $m_C$ is cathode weight.

$$E(\text{energy per volume unit}) = \frac{V_{dvp} \cdot q}{(t_A + t_{SS} + t_C) \cdot A} = \frac{1.1[V] \cdot 160 \cdot 10^{-3}[Ah]}{(0.025[cm] + 0.02[cm] + 0.047[cm]) \cdot 1.13[cm^2]} = 1692[Wh/l]$$

Where $V_{dvp}$ is discharge voltage plateau, $q$ is charge passing in the reaction, $t_A$ is anode thickness, $t_{SS}$ is anode thickness soaked with electrolyte separator thickness, and $t_C$ is cathode thickness.