Cell Performance of Ultra-Thin Polymer Cathode Cell Systems: Part II. Cation Intercalating Composite Polymer Cathode

Katsuhiko Naoi, William H. Smyrl and Boone B. Owens

Theoretical specific energy and power densities for thin film Li/LE or SPE/CP cell systems were calculated by modeling a bipolar-design polymer cathode rechargeable cell with hardware where LE, SPE and CP represent the liquid electrolyte (2M LiClO₄(PC)), solid polymer electrolyte (PEO₈LiX) and the conductive polymer (polypyrrole). The cell performance is obtained for a cation-intercalating PPy-PVS composite film which is composed of polypyrrole (PPy) into which has been incorporated the polymer anion, polyvinylsulfonate (PVS) during deposition. The energy and power densities are estimated as a function of cathode thickness (1 to 10⁵ μm), active cell area (1 to 10⁴ cm²) and the number of bipolar units (1 to 100). Compared to the anion-consuming polymer cathode system, significant enhancement of specific energy was achieved. The theoretical specific energy amounts to ca. 290 Wh/kg (bare cell) and ca. 209 Wh/kg for a bipolar Li/LE or SPE/PPy-PVS cell system (with hardware).
CELL PERFORMANCE OF ULTRA-THIN POLYMER CATHODE CELL SYSTEMS: 
PART II. CATION INTERCALATING COMPOSITE POLYMER CATHODE
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ABSTRACT
Theoretical specific energy and power densities for thin film Li/LE or SPE/CP cell systems were calculated by modeling a bipolar-design polymer cathode rechargeable cell with hardware where LE, SPE and CP represent the liquid electrolyte(2M LiClO_4(PC)), solid polymer electrolyte (PEO_9LiX) and the conductive polymer(polypyrrole). The cell performance is obtained for a cation-intercalating PPv-PVS composite film which is composed of polypyrrole(PPy) into which has been incorporated the polymer anion, polyvinylsulfonate(PVS) during deposition. The energy and power densities are estimated as a function of cathode thickness(1 to 10^-4 m), active cell area(1 to 10^4 cm^2) and the number of bipolar units(1 to 100). Compared to the anion-consuming polymer cathode system, significant enhancement of specific energy was achieved. The theoretical specific energy amounts to ca. 290 Wh/kg(bare cell) and ca. 209 Wh/kg for a bipolar Li/LE or SPE/PPy-PVS cell system(with hardware).

INTRODUCTION
Polymer cathode rechargeable cells, e.g., Lithium/polyaniline or Lithium/polypyrrole (PPy) in general are known to have a lower energy density when compared to inorganic insertion materials such as the oxides or sulfides of Ti, Mo and V_1^1. The main reason for this is the requirement of large mass/volume of electrolyte which is used to sustain the charge/discharge reaction because the cathodes show an anion-consuming reaction during the charging process^4. Electropolymerized conducting polymers, specifically PPy, shows cation-intercalating behavior when they are prepared with large polymeric anions, e.g., PSS^-, PVS^-, Nafion^5,6. Since the incorporated anions are immobilized during the oxidation/reduction process because of the steric hinderance, cations go in/out of the polymer film to maintain charge neutrality. The redox process for a PPy-PVS film would be as follows:

\[
\begin{align*}
\text{oxidation:} & \quad \left[\begin{array}{c}
\text{N} \\
\text{SO}_j \end{array}\right]_n + m M^+ \\
\text{reduction:} & \quad \left[\begin{array}{c}
\text{N} \\
\text{SO}_j \end{array}\right]_n \rightarrow m (M^+) m
\end{align*}
\]

Such composite cathodes(PPy/polymeric anion) can be utilized as higher energy cathode materials compared to the usual polypyrrole or polyaniline film with small monomeric anions as dopants. As already described in a prior report^3,4, a conducting polymer material
has very fast kinetics in exchanging electrons and ions during the charge/discharge process for very thin (of the order of microns) films, and this results in high power density.

The present paper reports the enhancement of the theoretical specific energy and power for a composite PPy-PVS cathode system in a lithium battery.

RESULTS AND DISCUSSION

Modeling of Cell

The electrode reactions (exchanging 1 Faraday of charge) for a cell which consists of a lithium anode, and a PPy-PVS composite film cathode are shown in Fig. 1. The maximum doping level (y) of the PPy-PVS composite cathode would be as follows;

\[ y = 100 \left( \frac{m}{n} \right) = 48.7 \]  

where \( \frac{n}{m} = 11.29 \) from the elemental analysis. The authors have assumed a maximum doping level of 45% for the present modeling study. For the cell reaction, one can use two types of electrolyte. One is a solid polymer electrolyte (SPE) and the other is a conventional liquid electrolyte (LE). PEO\(_8\)Li\(_X\)(X represent an anion) for SPE and 2 M LiClO\(_4\) (PC) for LE were chosen, respectively as the electrolytes. Also, a bipolar-design cell was assumed for more practical evaluation of the cell performance (see Fig. 2).

For a bare prismatic cell without hardware, the mass of each cell element, the energy density (ED) and the pulse power density (PD) are calculated as follows;

\[
W_c = W_{ppy} + W_{pa} \quad [3]
\]

\[
W_{ppy} = L_{ppy} S d_{ppy} \quad [4]
\]

\[
W_{pa} = \frac{y}{100} \frac{W_c}{M_{ppy}} M_{pa} \quad [5]
\]

\[
W_e = L_e S d_e \quad [6]
\]

\[
W_a = \frac{y}{100} \frac{W_e}{M_{ppy}} M_a \quad [7]
\]

\[
W_{cell} = W_c + W_a + W_e \quad [8]
\]

\[
ED = \frac{E_{ave} \left[ \frac{26.8W_{cy}}{100M_{ppy}} \right]}{W_{cell}} \quad [9]
\]

\[
PD = \frac{4\rho L_e}{W_{cell}} \quad [10]
\]

The values of ED and PD for the bare cell are plotted as a function of cathode thickness (see Fig. 3). The results are shown for the cells with SPE and LE electrolytes. The ED values for both SPE and LE configurations eventually amount to ca. 300 Wh/kg at the thickness of
over 1000 μm. For the SPE configuration, the ED value is more than 250 Wh/kg even for thin cathode film (less than 100 μm in thickness). In contrast with the LE cell, the specific energy falls toward zero as the cathode thickness goes to 1 μm because the electrolyte-separator combination is constant at 100 μm (see Fig. 4). With respect to the PD value, a similar trend is observed. The PD values decrease exponentially with the thickness of cathode, which have the range from about 10,000 to 0.0001 kW/kg when the thickness changes from 1 to 100,000 μm. Again, the cells with the cathode less than 100 μm in thickness, the difference in the PD values is significant. For thicker cells (>100 μm), the PD values for the SPE configuration are comparable to those of the LE configuration.

A more practical cell configuration would consist of the cell plus some basic hardware. The energy and power densities were calculated for a bipolar-design cell which consists of (X+1) cells in series. There are X bipolar cells plus the terminal electrodes: This type of cell reduces to a single prismatic cell design when the number of bipolar units are equal to 0. The following assumptions were made for this battery design and everything else is the same as in the preceding paper:

**Coulombic balance**

\[ Q_{Li} = 3Q_{cathode}(f_{ex} = 3) \]

**Hardwares**

<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
<th>Thickness</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC (terminal electrode)</td>
<td>Ni</td>
<td>25 μm</td>
<td>1 mm wider than R_{cell}</td>
</tr>
<tr>
<td>CC (bipolar unit)</td>
<td>Al</td>
<td>25 μm</td>
<td>1 mm wider than R_{cell}</td>
</tr>
<tr>
<td>Case</td>
<td>Synthetic resin</td>
<td>2 mm wider than R_{cell}</td>
<td></td>
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</table>

where R_{cell} is the radius of the circular cell.

**Thickness of electrolytes**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Thickness</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>LE</td>
<td>2 M LiClO_{4}(PC)</td>
<td>100 μm</td>
</tr>
<tr>
<td>SPE</td>
<td>PEO_{8}LiX</td>
<td>20% of cathode thickness (L_e &lt;100 μm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 μm (L_e ≥100 μm)</td>
</tr>
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</table>

Figure 4 shows the thickness variation of anode, electrolyte and cell as a function of cathode thickness for LE and SPE configurations. For the LE configuration, the electrolyte is assumed to be 100 μm, irrespective of the cathode thickness in order to avoid the shorting due to dendrite formation on the lithium anode. Therefore, the total cell thickness is mainly occupied by the electrolyte when the cell is thinner than 100 μm, and this results an essential disadvantage for the LE configuration. On the other hand, for the SPE configuration, the electrolyte can be made as thin as desired, even if the cell is thinner than 500 μm. In the SPE configuration, we assumed that the thickness of electrolyte was 20% of that of the cathode until it was 100 μm in thickness. The results was the configuration has advantage due to fewer electrochemical equivalents as the film becomes thinner.

On the basis of the above assumptions, the ED and PD values for a bipolar-design cell were calculated as a function of the number of bipolar units (X), the surface area of the active cell (S), and the cathode thickness (L_c). The ED and PD values for the unit cells (X=0; SPE configuration) are shown as functions of L_c and S (see Figs. 5 and 6). With respect to the surface area, the ED and PD values do not increase significantly over 100 cm² of cell area, which has also been shown for the Li/LE/polyaniline cell. Therefore, for further modeling, the cell area was fixed at 100 cm². The maximum values attainable for the ED
and PD values are 200 Wh/kg and 450 kW/kg when the cell includes the mass of the hardware.

**Bipolar Cell Results**

For the bipolar cells with X=5 and 50, the ED values are compared with a unit cell as a function of cathode thickness (see Fig.7). As X increases, the difference in ED between the LE and SPE configurations becomes significant. For the unit cell (X=0), the advantage of using SPE electrolyte is not remarkable. However, as X increases, the ED values for the SPE system becomes larger than those for the LE configurations.

Figure 8 shows the PD values for the same cell configurations as above. The PD values (0% DOD) are very sensitive to the thickness of cathode. Specifically, for the thin cell (Lc < 5 μm), the values for the SPE configuration are more than an order of magnitude larger than for the LE configurations. On the other hand, the LE configuration shows higher PD values (about 2 orders of magnitude higher) than the SPE configuration when the cathode is thicker than 100 μm. This result is due to the higher ionic conductivity for LE (6.0 x 10^-3 Ω^-1 cm^-1) than for SPE (10^-4 Ω^-1 cm^-1)²⁸.

**CONCLUSION**

Significant enhancement of the cell performance is calculated when a cation-intercalating polymer/polymer anion composite film is used as a cathode in a lithium secondary battery. The specific energy and power were estimated for Li/(SPE or LE)/PPy-PVS cells as a function of cathode thickness (1 to 105 μm), active cell area (1 to 10⁴ cm²) and the number of bipolar units (1 to 100). The maximum specific energy is more than doubled relative to an anion-consuming polymer cathode cell such as the Li/LE/Polyaniline cell. The theoretical specific energy is 290 Wh/kg (bare cell) and 209 Wh/kg for a bipolar Li/(LE or SPE)/PPy-PVS cell system (with hardware). The specific power is 50-100 kW/kg for LE and 500-5000 kW/kg for SPE configurations, respectively.

List of symbols (additional to PART I⁴)

- d_{ppy} (g cm⁻³): 1.48 (PPy)
- d_{e} (g cm⁻³): 1.30 (2M LiClO₄/PC)
- d₃ (g cm⁻³): 0.53 (Li)
- E_{ave} (V): 3.0 (0% DOD)
- E_{oc} (V): 3.8 (excess factor)
- f_{ex} (-): 3.0 (thickness of electrolyte/seperator)
- L_{e} (cm): 100 x 10⁻⁴
- L_{c} (cm): 1, 10, 100 x 10⁻⁴
- L_{ppy} (cm): 1, 10, 100 x 10⁻⁴
- M_{a} (g mol⁻¹): 6.94 (Li)
- M_{pa} (g mol⁻¹): 107 (VS)
- M_{py} (g mol⁻¹): 65 (pyrrole)
- y (%): 45
References


(d) K. Naoi, A. Ishijima and T. Osaka, *J. Electroanal. Chem.*, 217, 203 (1987);


Cathode: 
\[
\begin{align*}
\text{Li}^+ + e^- &\quad \text{charge} \\
\text{Li}^+ &\quad \text{discharge}
\end{align*}
\]

Anode: 
\[
\begin{align*}
\text{Li} &\quad \text{charge} \\
\text{Li}^+ + e^- &\quad \text{discharge}
\end{align*}
\]

Fig. 1 Cathode and anode reactions for Li/PPy-PVS cell.

Fig. 2 Cell construction of a bipolar-design Li/LE or SPE/PPy-PVS cell.
Fig. 3 Specific energy and power for a bipolar unit (Li/LE or SPE/PPy-PVS cell) without hardware.
Fig. 4  Thickness changes for anode, electrolyte, cell as a function of cathode thickness.
Fig. 5 Specific energy vs. cell area and thickness of cathode for Li/SPE/PPy-PVS cell (X=0).

Fig. 6 Specific power vs. cell area and thickness of cathode for Li/SPE/PPy-PVS cell (X=0).
Fig. 7  Specific energy vs. thickness of cathode for Li/SPE or LE/PPy-PVS cells (S=100 cm²; X=0, 5, 50).
Fig. 8  Specific power vs. thickness of cathode for Li/SPE or LE/PPy-PVS cells ($S=100 \text{ cm}^2$; $X=0$, 5, 50).
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<tr>
<td>1</td>
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<td>SPE, Polyaniline</td>
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<td>References</td>
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