Flexible Thin-Film Battery based on Graphene-Oxide Embedded in Solid Polymer Electrolyte

Supporting Information

Mejdi Kammoun, Sean Berg and Haleh Ardebili*

*Department of Mechanical Engineering, Engineering Building 1, University of Houston, Houston, TX 77204-4006, USA. E-Mail: <u>hardebili@uh.edu</u>

	Battery 1	Battery 2	Battery 3	Battery 4			
Electrode (Anode/ Cathode*)/ Weight (g)	Graphite (0.032 g)/ LiCoO ₂ (0.09g-0.08g)						
Current Collector (Thickness)	Cu (9 µm)/Al Foil (15 µm)						
Electrolyte	PEO	PEO	PEO+1 wt% GO	PEO+1 wt% GO			
Weight (g)	0.2997	0.2816	0.2913	0.2973			
Plasticizer** Weight (%)	0.0211g (7%)	0.0158g (6%)	0.0132g (5%)	0.0171g (6%)			
Seal Type	Plastic Seal Lamination						
Battery Dimension (L×W×T) (mm)	20.47×20.53×0.742	20.54×20.18×0.732	21.25×21.24×0.722	20.65×20.76×0.778			
Battery Weight (g)	1.125	1.132	1.418	1.045			
Average Capacity (mAh/cm ²)	0.084	0.099	0.093	0.129			
Capacity Fading (%)	31%	25%	51%	12%			
Output Voltage (V)	2.787	2.800	2.910	2.870			
Energy Density (mWh/cm ³)***	3.173	3.821	3.742	4.757			
(Wh/kg)	0.837	0.988	0.762	1.417			
Power Density (mW/cm ³)****	9.391	9.563	10.076	9.222			
(W/kg)	2.477	2.473	2.053	2.748			
Bending Radius (mm)	Flat	18.9	Flat	18.9			

Table S1: Material properties and performance of flexible LIB

*LiCoO2: Density (200-225 g/m²)

Graphite: Density (80 g/m²)

**LiPF6: Density (1.22 g/ml at 25°C)

*** Energy Density= Average Capacity (mAh/cm²)* Output Voltage (V)/ Total thickness of the battery (cm)

**** Power Density=Current (mA)* Output Voltage (V)/ Total thickness of the battery (cm)

Finite Element Analysis

Finite element analysis (FEA) was conducted to model the bending of the battery using Abaqus 6.13-5 software. This software package offers extensive element, material modeling and contact formulation options. The layers of the battery were stacked initially in contact and modeled as a 20x20 mm² area section. The thicknesses of each battery layer and the materials were modeled based on the experiment, and a linear elastic material model was created. Two different solid polymer electrolytes were modeled numerically: PEO and PEO/1 wt% GO. The finite element analysis was performed for the lamination/encapsulation followed by bending.

All layers besides the electrolyte were modeled with CPS4I elements. These elements contain additional shape functions that allow the bending curvature and strain field of each element to accurately model the deflection. Mesh refinement was completed to ensure that the bending for the modeled radius was accurate. The electrolyte was modeled using CPS8 elements, which are quadratic full integration elements capable of properly modeling bending, and are not susceptible to locking like first order elements during the high deflection experienced from the lamination step due to the low stiffness of the electrolyte material. The interactions between each layer, with the exception of the layers. The electrolyte contact was modeled as frictionless, between the electrolyte/anode and electrolyte/cathode layers, in order to minimize the addition of shear stress between the layers and any axial stress from lateral expansion during compression. This expansion was thought to be significant since the electrolyte material is much less stiff than the other materials.

The lamination/encapsulation of the battery produces initial compressive stresses in the battery layers. The final thickness of the battery with each type of electrolyte is 0.75mm. The battery is compressed in the initial steps of the analysis using a combination of displacement, followed by surface pressure to maintain the thickness in the battery of 0.75mm. It is noted that the contact pressure between the layers is greater in the battery with the composite electrolyte, compared to that of pure PEO based battery. The lamination process results in a final measured battery thickness of 0.75mm in both batteries after lamination. Since the composite electrolyte is initially thicker than the PEO electrolyte, more compression is required to produce the final 0.75mm thickness for the composite electrolyte, which causes increased contact pressure. Furthermore, since the composite material is stiffer and has a higher elastic modulus than the PEO electrolyte battery to the final lamination thickness, which is accompanied by a further increase in the contact pressures after lamination.

The finite element analysis of the LIB bending was carried out after the encapsulation process, in order to account for the real effects associated with the lamination compression. No delamination is predicted to occur for a bending radius of 17 mm, verified through experiment. The FEA results show that the contact pressure increases as the bending is applied to the flexible battery.

Materials	E (MPa)	v
Aluminum	68947.6	0.334
Copper	117210.9	0.355
Laminate	4895.3	0.38
LiCoO ₂	135800	0.306
Graphite	14665	0.2355
PEO	10.82	0.3
PEO/1 wt% GO	33.45	0.3

Table S2: Materials Properties used in FEA



Figure S1. Lamination process: (a) first layer and (b) second layer lamination.







Figure S2 (a) Impedance spectra of bent flexible LIB based on pure PEO and PEO/1 wt% GO, under fixed bending radius of 18.9 mm in fresh condition, (b) impedance spectra of flexible LIB based on pure PEO and PEO/1 wt% GO, in flat position, compared in the first charge/discharge cycle and (c) after 100 cycles (repeated in larger size from Figure 2b and 2c) at 1 mA (~2C) from 2.0 V – 4.9 V at room condition.



Figure S3. Discharge capacities of three flexible batteries based on PEO, at 1mA (2C)

from 2.0 V - 4.9 V at room condition.



Figure S4. Discharge capacities of three flexible batteries based on PEO/1wt%GO at

1mA (2C) from 2.0 V - 4.9 V, at room condition.



Figure S5. Discharge capacities of PEO and PEO/1wt%GO based flexible batteries averaged over 3 battery units, at 1mA (2C) from 2.0 V - 4.9 V at room condition.

The capacity retention of the flexible LIB at different current rates is displayed in **Figure S6**. The electrochemical performance of the LIBs can be attributed to the structural and electrochemical stability of the polymer-based electrolyte. Even at the current rate of 1.1mA (~2.2C), the flexible battery based on the polymer nanocomposite electrolyte in bending position can deliver high discharge capacity of 0.122 mAh cm⁻² after 50 cycles. This is far superior to the battery based on pure PEO, which exhibits a capacity of 0.059 mAh cm⁻² after 50 cycles.



Figure S6. Capacity retention of the flexible LIB in flat and bending configurations at different current rates (25 cycles per rate) at \sim 2C (1mA), \sim 1C (0.5 mA) and \sim 0.6C (0.3 mA), from 2.0 V- 4.9 V at room condition.

The behavior of the charge and discharge cycling for the four different batteries is presented in **Figure S7**. The plot shows that the capacities for all batteries decrease but at different rates of fading. For example, the capacity varies from 0.091 mAh cm⁻² for the flat battery based on the pure PEO film to 0.141 mAh cm⁻² for battery using the same electrolyte but in bending position during the first cycle. Further charge-discharge cycles resulted in capacities of 0.065 mAh cm⁻² and 0.087 mAh cm⁻² with 31% and 25% capacity fading between the first and the last cycles for flat battery and bent battery with pure electrolyte, respectively. The capacity fading in Li ion batteries is generally caused

by the loss of primary active material (Li+) and it can be attributed to lithium metal deposition, electrolyte decomposition, active material dissolution, phase transition of electrode materials, and passive layer formation on the electrode and current collectors. ^[1-3] From **Table S1**, the highest values of capacity fading are associated with the batteries made with pure polymer electrolyte. This suggests that the GO fillers may increase the electrolyte stability and improve the battery cyclability.



Figure S7. Charge and discharge behavior of thin-film LIBs at the 1st and 100th cycle for (a) flat battery (PEO), (b) bent battery (PEO), (c) flat battery (PEO/1 wt% GO), and (d) bent battery (PEO/1 wt% GO).



Figure S8. (a) Discharge capacity retention as a function of bending state and electrolyte type at a constant current rate of 1 mA during 100 cycles, and **(b)** coulombic efficiencies of the flexible batteries.

The capacities of four batteries made with composite electrolyte with different percentages of GO filler under fixed bending radius are shown in **Figure S8**. **Figure S8a** indicates that the highest capacities were recorded for the batteries made of electrolyte with 1 wt% GO. All batteries that are in bending position show higher average capacities compared to the flat batteries based on the same electrolyte. The flat battery using the electrolyte with minimum filler percentage (0.5 wt% GO) exhibits the lowest capacity and it shows similar behavior to the battery made with pure electrolyte. The batteries made with 1 wt% GO composite electrolyte exhibit the highest capacity compared to the other composite electrolyte under the same testing conditions. Adding GO particles to the polymer electrolyte can enhance the bulk conductivity which can affect the capacity of the flexible battery ^[4]. GO particles reduce the crystallinity of PEO, and the highly

amorphous structures can better facilitate ion transport in polymer electrolytes. Adding high percentage of nanofiller may decrease the ionic conductivity of polymer electrolyte due to adverse effects like aggregation, blocking and ion trapping. Therefore, relatively low filler content (i.e. 1 wt% GO) can ensure optimal ion conductivity. **Figure S8b** presents the coloumbic efficiency of the four flexible batteries. All flexible batteries demonstrate highly stable efficiencies (higher than 91% after stabilization) under the same testing conditions.

The comparative adhesion between the different layers of the thin film battery was investigated through the method of shear by tensile loading. After disassembling the battery, high strength bonding tape (3M VHB Tape) was used to fix the two layers in question to the self-tightening wedge grips of a motorized mechanical testing stand Mark-10-ESM301L. The results of the test (at peeling speed of 1 mm/minute) are presented in **Figure S9**. According to **Figure S9 a and b**, the highest maximum load applied before sliding/shear was recorded between the electrode layer (LiCoO₂) and the current collector (AI) and the lowest load was noted between the two encapsulant layers. A good adhesion between the electrode layer (LiCoO₂)/the current collector (AI) and electrode layer (LiCoO₂)/the current collector (AI) and electrode layer (CiCoO₂)/the current collector (AI) and electrode layer (LiCoO₂)/the current collector (AI) and electrode layer (Graphite)/the current collector (Cu), no shear/sliding could be observed at the maximum tension load applied by the machine (marked by * in **Figure 9a**).



Figure S9. (a) Maximum tension load recorded before sliding/shear occurs and **(b)** displacement load profile between the different layers of the thin film battery.

Table S3: Comparison of the electrochemical performances of flexible thin-film

Year	Reference	Electrode (Cathode/ Anode)	Electrolyte	Percentage Liquid (wt%)	Capacity	Capacity Fading (%)	Cycles Reported	Current Density	Operating Voltage
2013	Wei et al [23]	Graphene/ Lithium Foil	Polymer electrolyte (PEG- borate ester)	No Liquid	0.02 mAh/cm ²	50%	100	100 µA/cm ²	0.0 to 3.0 V
2011	Yang et al [24]	$\begin{array}{c} LiMn_2O_4/\\ Li_4Ti_5O_{12}\end{array}$	Transparent gel membrane (1 M LiClO ₄ in EC/DEC and PVDF-HFP)	Not Specified	80 mAh⁄g	20%	15	100 µA/cm ²	1.5 to 3.0 V
2013	Xu et al [25]	LiCoO ₂ / Li ₄ Ti ₅ O ₁₂	Gel electrolyte (100 g LiClO₄, 500 ml EC, 500 ml DMC and 10 g PEO	~ 90 wt% *	1.1 mAh/cm ²	27%	20	Not Specified	1.6 to 2.5 V
2012	Koo et al [26]	LiCoO2/ Lithium	Lithium phosphorus oxynitride electrolyte (LiPON)	No Liquid	0.106 mAh/cm ²	1.6%	100	46.5 μA/cm ²	3.0 to 4.2 V
2015	This Study	LiCoO ₂ / Graphite	Polyethylene Oxide/ LiClO ₄ /1wt%GO+drops of	5-7 wt%	0.13 mAh/cm ²	9%	20	- 250 µA/cm ²	2.0 to 4.9 V
			EC/DMC (added during battery assembly)			42%	100		

lithium ion batteries

* This value was estimated based on the provided weight and volume of the electrolyte components and the densities of EC and DMC.

Movie S1: LIB under mechanical cyclic bending test.

References

(1) G. Ning, B. Haran, B. N. Popov, Journal of Power Sources 2003, 117, 160.

(2) P. Arorata, R. E. White, M. Doyle, J. Electrochem. Soc., 1998, 145, 3647.

(3) D. Zhang, B.S. Haran, A. Durairajan, R.E. White, Y. Podrazhansky, B. N. Popov, Journal of Power Sources 2000, 91, 122.

(4) M.Yuan, J. Erdman, C. Tang, H. Ardebili, RSC Advances 2014.