Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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ASSOCIATED CONTENT

Supporting Information

Zero Fire Battery Concept : Water-in-Battery

Suppression of the fire element (oxygen, ignition point) by water

Water can block the fire by controlling two elements (oxygen and suppressing to reach the ignition points). The following calculations show why water is an effective option for suppressing fire in a WiB system.

At first, Table.1 and Table. 2 calculate the amount of oxygen required for combustion and chemical reactions caused by thermal runaway of LFP (lithium iron phosphate battery) (3.3 V / 1.1 Ah / 18650) and NCA (lithium nickel cobalt aluminium oxides) (3.7 V / 3.4 Ah / 18650) cell each. It is divided into anode, cathode, separator, and electrolyte parts, with an oxygen content of 809.4 mmol, and 1119.0 mmol required for full combustion. At room temperature of 1 atm, the dissolved oxygen in the water is 0.3 mmol/L, while the average oxygen in the atmosphere is about 7.9 mmol/L, which is about 26 times higher. Compared to the atmosphere, where oxygen can be continuously supplied, the amount of oxygen contained in the water required for full combustion of the battery is extremely limited, making it suitable to prevent fire start.

Also, the water has about four times higher specific heat (4.18 J/g°C) compared to commonly used battery extinguishing agents. In addition, if the maximum temperature of water required to suppress thermal runaway is set to 100 °c, it can include not only the thermal energy required for temperature rise, but also the energy required for phase shift (2257 J/g) for battery cooling. This indicates that water can inhibit the ignition point required for combustion.

In the WiB system, the battery was embedded in water. Therefore, air, which contains oxygen, is restricted, and water, directly in contact with the battery, works as an effective coolant for fire prevention.

Experimental Section - Amount of Water Calculation

The theoretical amount of water needed to block fire in the WiB system is calculated by the amount of water needed to block oxygen and prevent it from reaching the ignition point. As the required oxygen needed for fire is extremely small in water, the theoretical amount of water needed in WiB is calculated as the heat released during the battery thermal runaway.

The calorific value of the battery thermal runaway can be calculated by Hatchard et al. based on the Arrhenius equation. It is based on the equation of specific heat release (Joule per gram of material), the volume of specific contents, and reaction parameters, determined by the decomposition factor and activation energy of the materials comprising the battery. Based on these values, the total heat release is calculated by the reactions of the positive and negative solvent reactions, and decomposition reactions of the solid electrolyte interface and electrolyte. The cell with 3.7 V, 2.6 Ah, and 18650 type had heat release about 17.9 kJ to 26.2 kJ. They were varied by producers such as Sanyo, Sony, Samsung, and LG.

To standardize the theoretical amount of the required water, the maximum energy that can be generated in the short circuit is converted into heat energy, which can raise the temperature of the water. The heat absorbance of the water was calculated by multiplying the specific heat capacity of the water (4.18 J/g°C), temperature changes from room temperature (25°C) to the boiling point of water (100°C), and the amount of water. The energy required for the phase change was not considered in this equation. The theoretical amount of water needed is approximately 12.2 mL/Wh. In this case, the cell with 3.7 V, 2.6 Ah, and 18650 releases approximately 34.6 kJ of heat, and the amount of water needed is approximately 117 mL. The WiB used in Fig. 2(a) requires 77 ml of water.

The functional elements of WiB system may decrease the energy density of the battery system. However, the ratio of water needed in the system largely decreases when it is applied in a large size ESS. By blocking the thermal runaway propagation through the concept of WiB system by water penetration, the water needed in the system largely decreases in the large size of the ESS system. The numercial value of the propagation ratio would research more detail in the next paper. The ratio of battery and water is explained more in Figure S4.

Experimental Section - Normal Cycle of the Water-in-Battery

The electrochemical performances of the normal LIB and WiB cell were compared to check the operation appearance. A pouch-type lithium polymer secondary battery (3.7 V / 1.7 Ah) was driven and immersed in approximately 77 mL of water. The cycle is performed at a 0.3 C-rate which is a typical solar-connected ESS operating ratio. The voltage curves of the normal LIB and WiB single cell were almost identical until the 200th cycle. This shows that water does not destroy the WiB cell system.

Supplementary properties of the water - Freezing and Heat transfer

The properties of the water could be both advantages and disadvantages for the operation of the WiB system. For first, when ESS is exposed to cold temperature in the water, it has the possibility to freeze the water and damage the batteries. However, the amount of heat generation from the batteries is always large enough that we have to focus on cooling even in the winter. Also freezing issue of the water can easily be prevented at a low cost by circulating water inside the ESS or supplying the hot water. Due to the circulation of water, the kinetic energy of one water molecule is greater than the binding energy by van der Waals, which means crystals cannot be maintained. In addition, we are developing on the substitute of the water composed of NaCl with the seawater and polymer for expanding the concept of WiB into the marine application and suppressing the fire more efficiently. Additionally, we are manufacturing the ESS Module for having extra space for preparing the abuse condition.

The high heat capacity of water (4.18 J/g°C) has advantages for the low increase of temperature when WiB is exposed in high temperature, while the low decrease of temperature may expose cell into high temperature. To say again, the water is difficult to cool, and at the same time it is difficult to be hot cause of the heat capacity. By the WiB system, lowering the average operation temperature is possible, while protecting the battery to reach the high temperature for protecting thermal aging and performances increase in high temperature.

LFC Cell (Voltage : 3.32 V / Norminal Capacity :1.1 Ah / 18650)

Components	Mass ratio	Mass (g)	Formula	M (g mol⁻¹)	n (mmol)	Li-capacity (Ah)	Reaction with O2 (Thermal Runaway)	Oxygen	n (mmol) O2	Reference
Cathode coating :										
Active material	80.0%	7.73	$Li_{0.882}FePO_4$	156.9	49.2	1.32	(1-x)LiFePO4 + xFePO4 -> (1-x)LiFePO4 + 0.5xFe2P2O7 + 0.25O2 [x = 0.882]	Producing	12.3	P. Huang, Q. Wang, K. Li, P. Ping and J. Sun, *Sci. Rep.*, 2015, **5**, 7788
Particle coating	10.0%	0.97	C	12.0	80.5		C + O2	Consumming	80.5	C.-Y. Wen, C.-Y. Jhu, Y.-W. Wang, C.-C. Chiang and C.-M. Shu, J. Therm. Anal. Calorim., 2012, 109, 1297–1302
Carbon black	5.0%	0.48	C	12.0	40.2		C + O2	Consumming	40.2	C.-Y. Wen, C.-Y. Jhu, Y.-W. Wang, C.-C. Chiang and C.-M. Shu, J. Therm. Anal. Calorim., 2012, 109, 1297–1302
Binder (PVDF)	5.0%	0.48	$(C_2H_2F_2)_n$	64.0	7.5		2C2H2F2 + 5O2 -> 4CO2 + 2H2O + 2F2	Consumming	18.8	Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge
Sum	100%	9.66							127.2	
Anode coating:										
Graphite	93.5%	4.84	$Li_{0.006}C_6$	72.1	67.2	1.80	Li0.006C6 + 6.008O2 -> 0.006(LiO2) + 6(CO2)	Consumming	403.2	
Binder (CMC)	5.0%	0.26	$(C_{7.4}H_{10.7}O_{6.4})_n$	202.1	1.3		CMC + 3.175O2 -> 7.4CO + 5.35H2O	Consumming	4.1	Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge
SEI, lithium fluoride	0.4%	0.02	LiF	25.9	0.8		$LiF + 1.5O_2 \rightarrow LiFO_3$	Consumming	1.2	D. Doughty and E. P. Roth, Electrochem. Soc. Interface, 2012, 21, 37–44
SEI, lithium carbonate	1.1%	0.06	Li_2CO_3	73.9	0.8		$Li_2CO_3 + 0.5O_2 \rightarrow Li_2O + CO_3$	Consumming	0.4	D. Doughty and E. P. Roth, Electrochem. Soc. Interface, 2012, 21, 37–44
Sum	100.0%	5.18							408.4	
Separator:										
PP	66%	0.76	$(C_3H_6)_n$	42.1	18.0		C3H6 + 6O2-> 3CO2 + 6H2O	Consumming	108.0	
PE	34%	0.39	$(C_2H_4)_n$	28.1	13.9		C2H4 + 4O2-> 2CO2 + 4H2O	Consumming	55.6	
UHMWPE	—	—	—	—	—				-	
Sum	100%	1.15							163.6	
Electrolyte:										
SEI, polymer organic	2.0%	0.13	$(C_6H_4O_6)_n$	172.1	0.7		C6H4O6 +2O2 -> 6CO + 2H2O	Consumming	1.4	Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge
SEI, organic	3.9%	0.25	$(CH_2OCO_2Li)_2$	162.0	1.5		(CH2OCO2Li)2-> Li2CO3 + C2H4 + CO2 + 0.5O2	Producing	0.8	J. Jeevarajan, in Lithium-Ion Batter. Adv. Appl., Elsevier, 2014, pp. 387–407
EC	24.8%	1.59	$C_3H_4O_3$	88.1	18.1		EC + O2 -> 3CO + 2H2O	Consumming	18.1	Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge
DMC	33.0%	2.12	$C_3H_6O_3$	90.1	23.5		DMC + 1.5O2 -> 3CO + 3H2O	Consumming	35.3	Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge
EMC	16.5%	1.06	$C_4H_8O_3$	104.1	10.2		EMC + 4.5O2-> 4CO + 8H2O	Consumming	45.9	Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge
PC	8.3%	0.53	$C_4H_6O_3$	102.1	5.2		PC +2O2 -> 4CO + 3H2O	Consumming	10.4	
MPC	—	—	—	—	—		-	-	-	
Salt	11.5%	0.74	$LiPF_6$	151.9	4.9		$LiPF_6 + H_2O \rightarrow 2HF + LiF + POF_3$	-	-	D. Doughty and E. P. Roth, Electrochem. Soc. Interface, 2012, 21, 37–44
Sum	100.0%	6.41							110.2	

Inactive components :										
Housing (metal can)		10.45								
Cathode Al foil		2.14								
Anode Cu foil		3.86								
Other components		—								
Sum		16.46								
Total sum		38.87							809.4	

Table S1. Reaction with Oxygen while Thermal Runaway by LFP Battery Component

NCA Cell (Voltage : 3.68 V / Norminal Capacity :3.35 Ah / 18650)

Components	Mass ratio	Mass (g)	Formula	M (g mol⁻¹)	n (mmol)	Li-capacity (Ah)	Reaction with O2 (Thermal Runaway)	Oxygen	n (mmol) O2	Reference
Cathode coating:										
Active material	95.0%	17.04	$Li_{0.925}(Ni_{0.80}CO_{0.15}Al_{0.05})O_2$	95.6	178.2	4.78	Lix(Ni0.80Co0.15Al0.05)O2 -> Lix(Ni0.8.Co0.15Al0.05)O1+x + 0.5(1-x)O2 [x=0.925]	Producing	6.7	P. Ping, Q. Wang, P. Huang, K. Li, J. Sun, D. Kong and C. Chen, J. Power Sources, 2015, 285, 80–89
Particle coating	—	—	—	—	—		-			
Carbon black	2.5%	0.45	C	12.0	37.4		C + O2	Consumming	37.4	C.-Y. Wen, C.-Y. Jhu, Y.-W. Wang, C.-C. Chiang and C.-M. Shu, J. Therm. Anal. Calorim., 2012, 109, 1297–1302
Binder (PVDF)	2.5%	0.45	$(C_2H_2F_2)_n$	64.0	7.0		2C2H2F2 + 5O2 -> 4CO2 + 2H2O + 2F2	Consumming	17.5	Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge
Sum	100%	17.93							48.2	
Anode coating:										
Graphite	93.5%	10.92	$Li_{0.008}C_6$	72.1	151.5	4.06	Li0.008C6 + 6.008O2 -> 0.008(LiO2) + 6(CO2)	Consumming	910.2	
Binder (CMC)	5.0%	0.58	$(C_{7.4}H_{10.7}O_{6.4})_n$	202.1	2.9		CMC + 3.175O2 -> 7.4CO + 5.35H2O	Consumming	9.2	Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge
SEI, lithium fluoride	0.4%	0.04	LiF	25.9	1.7		LiF + 1.5O2 -> LiFO3	Consumming	2.6	D. Doughty and E. P. Roth, Electrochem. Soc. Interface, 2012, 21, 37–44
SEI, lithium carbonate	1.1%	0.13	Li_2CO_3	73.9	1.7		Li2CO3 + 0.5O -> Li2O + CO3	Consumming	0.9	D. Doughty and E. P. Roth, Electrochem. Soc. Interface, 2012, 21, 37–44
Sum	100.0%	11.67							922.9	
Separator:										
PP	—	—	—	—	—					
PE	—	—	—	—	—					
UHMWPE	100%	0.70	$(C_2H_4)_n$	28.1	25.0		C2H4 + 4O2-> 2CO2 + 4H2O	Consumming	100	
Sum	100%	0.70							100	
Electrolyte:										
SEI, polymer organic	2.0%	0.09	$(C_6H_4O_6)_n$	86.1	1.0		C6H4O6 +2O2 -> 6CO + 2H2O	Consumming	2	Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge
SEI, organic	12.7%	0.56	$(CH_2O_CO_2Li)_2$	162.0	3.5		(CH2OCO2Li)2-> Li2CO3 + C2H4 + CO2 + 0.5O2	Producing	1.8	J. Jeevarajan, in Lithium-Ion Batter. Adv. Appl., Elsevier, 2014, pp. 387–407
EC	17.1%	0.75	$C_3H_4O_3$	88.1	8.5		EC + O2 -> 3CO + 2H2O	Consumming	8.5	Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge
DMC	49.7%	2.19	$C_3H_6O_3$	90.1	24.3		DMC + 1.5O2 -> 3CO + 3H2O	Consumming	36.5	Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge
EMC	5.3%	0.23	$C_4H_8O_3$	104.1	2.2		EMC + 4.5O2-> 4CO + 8H2O	Consumming		Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge
PC	—	—	—	—	—		-	-	-	
MPC	2.7%	0.12	$C_8H_8O_3$	196.1	0.6		MPC(liquid) +4.5O2 -> 8CO + 4H2O	Consumming	2.7	Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge
Salt	10.6%	0.46	$LiPF_6$	151.9	3.1		$LiPF_6 + H_2O \rightarrow 2HF + LiF + POF_3$	-	-	D. Doughty and E. P. Roth, Electrochem. Soc. Interface, 2012, 21, 37–44

Sum	100.0%	4.41							47.9	
Inactive components:										
Housing (metal can)		5.71								
Cathode Al foil		1.20								
Anode Cu foil		2.72								
Other components		1.05								
Sum		10.69								
Total sum		45.40							1119	

Table S2. Reaction with Oxygen while Thermal Runaway by NCA Battery Component

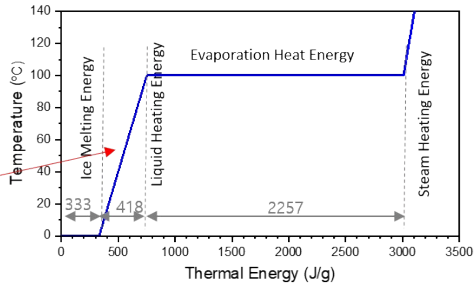
❖ Oxygen Needed for Thermal Runaway

	Voltage (V)	Norminal Capacity (Ah)	Cell Type	Oxygen Need for Complete Combustion (mmol)				
				Cathode	Anode	Separator	Electrolyte	Sum
LFP	3.32	1.1	18650	127.2	408.4	163.6	110.2	**809.4**
NCA	3.68	3.35	18650	48.2	922.9	100	47.9	**1119**

	Oxygen (mmol/L)
Air	**7.9**
Water	**0.3**

❖ Heat Absorbance Capacity of the Water

Substance	Chemical Formula	Cp in J/g°C	Relative heat capacity
Halon 1211	CF_2BrCl	0.753	
Halon 2402	$C_2F_4Br_2$	0.753	
Halon 104	CCl_4	0.794	
Halon 1301	CF_3Br	0.794	
Carbon Dioxide	CO_2	0.832	
Dry Powder(BC)	$NaHCO_{3\,(s)}$	1.042	
NOVEC 1230	$C_6F_{12}O$	1.103	
HFC 125	C_2HF_5	1.260	
Water	$H_2O_{\,(l)}$	**4.184**	



❖ Standard Set for Theoretical Amount of Water

Maximum Energy of Lithium Ion Battery

: E (Wh) × 3,600 $\frac{J}{Wh}$ = Q (kJ)

Heat absorbance of the water (25°C → 100°C)

: 4.2 $\frac{kJ}{kg\cdot°C}$ $(Heat\ capacity\ og\ the\ water)$ × m(water mass) × $75^{o}C$

Fig S1. (a) Oxygen needed for thermal runaway (b) Thermal Energy absorbency of the water

➢ WIB Sample

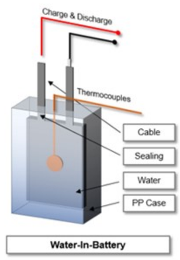
Li-Polymer 1S1P
DTP 505060
(3.7V / 1700mAh)
LiC/Polyacrylonitrile /LiPF6/$LiCoO_2$

Component	Material	Information
Cable	Ni Tab	0.15T x3x120mm
Case	PP	3T x90x70x14mm
Water	H2O	77mL (for Cycle) 1L (for Abuse Test)
Sealing	Laminator	DNP D-EL408PH(3) (PET + ALM + PP)
	Sealant	DNP PPs-N100(N) (PP + PEN)
	Heat Sealing (220 °C, 15s)	

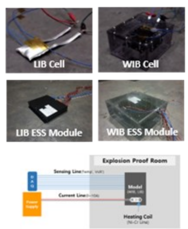
Li-Ion 14S18P
LG 18650 LM-MOTOR
(DC 50V / 52Ah)
LCO/LTO /Organic Electrolyte

Component	Material	Information
Cable	Cu	4.8 pi
Case	PP	10T x67x60x30cm
Water	H2O	96 L
Sealing	Protection Case	Glass Fiber (3M -8915) + Heat Shrink Tube + Kapton Tape + PC(0.5t)
	Water Proof	Laminator + Sealant Epoxy(EPONS ES-2)
	Winding -> Hot Sealing -> Degassing -> Packing	

➢ WIB Test Condition & Environment



Cycle Test	Normal	Extreme
Temperature	24 °C	40 °C
Charge	0.3C	1C
Discharge	0.3C	3C
Voltage Cut	2.8V / 4.2V	
Rest	10min	
Equipment	 Wonatech WBCS3000HP12 10V/20A/8Ch	 Graphtec GL- 240 Ch20



KTL (Korea Testing Laboratory)

Abuse Test	Over charge	Over heating
Condition	3C	350 °C
Measure	Voltage & Temp	
Phenomena	Thermal Runaway	
Equipment	 Kikusui ICP20180407 30V / 10A	 Graphtec 20210027 Ch20

Fig S2. Materials and test environments of WIB

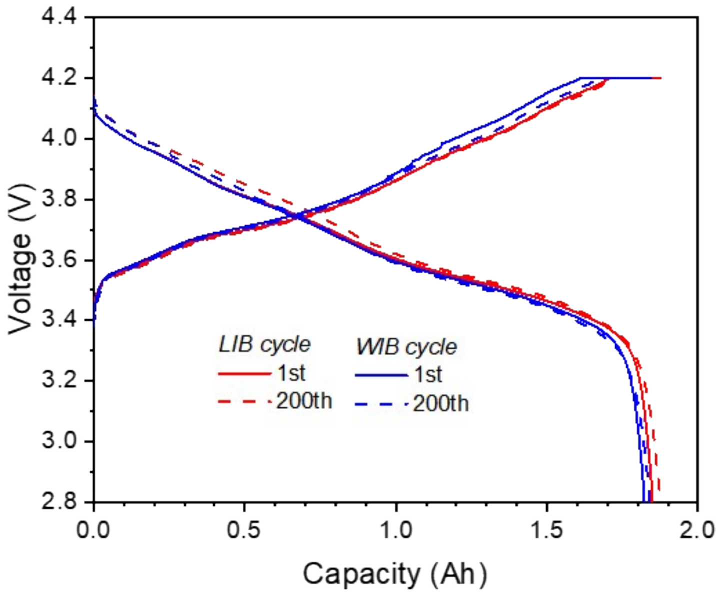


Fig S3. Normal Cycle of LIB and WIB (0.3C-rate)

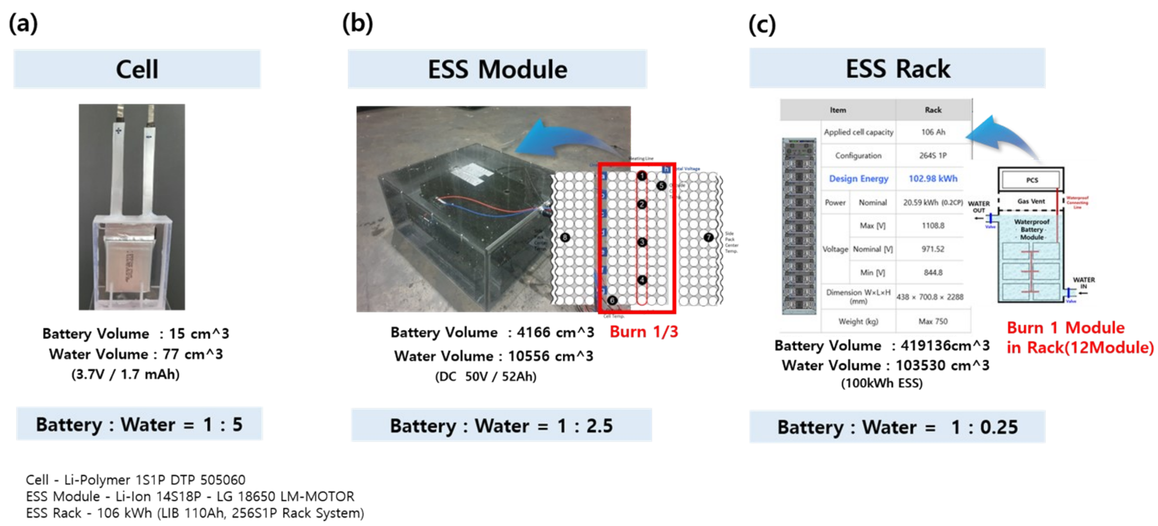


Figure S4. Volume ratio of battery and water of WiB (a) lithium pouch cell (3.7 V, 1.7 Ah), (b) ESS Module (50 V, 52 Ah), (c) ESS Rack (100 kWh composed of 12 Module (81 V, 106 Ah))

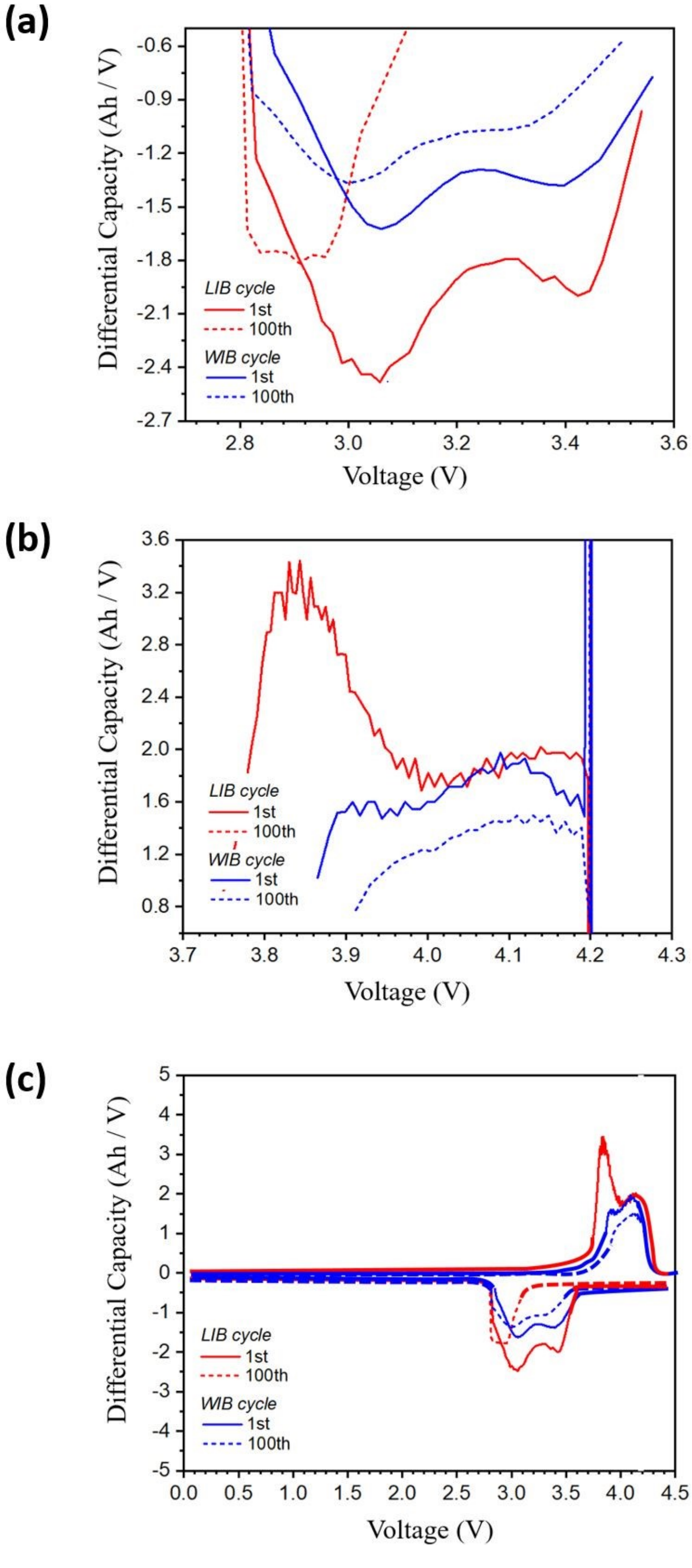


Figure R5. (a) Differntial Capacity plots (dQ/dV) of the 1st and 100th cycle of WiB and LIB cell in high C-rate and temperature of (a) discharge process, (b) charge process, and (c) artificial graph based on the results

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