Electronic Supplementary Information

for *J. Mater. Chem. A*, DOI: 10.1039/x0xx00000x ((will be completed by the editorial staff))

Improved Cycle Lives of $LiMn_2O_4$ Cathodes in Lithium Ion Batteries by an Alginate Biopolymer from Seaweed

By *Myung-Hyun Ryou, Seonki Hong, Martin Winter, Haeshin Lee,* and Jang Wook Choi**

1. Materials and their preparation

Alginate sodium salt (Protanal® LF 10/60, FMC Biopolymer, USA) was purified by exhaustive dialysis (MWCO = 25 kDa) in DI water until a yellowish color was dispelled. The dialysed alginate in white powder form was obtained by lyophilization, and the absence of impurities was confirmed by ultraviolet-visible (UV-Vis) measurements.[S1] Dialysis membranes were purchased from SpectraPor (USA) and rinsed with DI water several times before use. PVDF (Kynar 741, Arkema Inc., USA) manganese (II) chloride ($MnCl_2$, Sigma Aldrich, USA), manganese perchlorate solution ($Mn(ClO_4)_2$•xH_2O, 99%, Aldrich, USA), 1_M of $LiClO_4$ in a mixture of ethylene carbonate/propylene carbonate (EC/PC, 1:1 v/v, PANAX ETEC Co. Ltd, Korea), 1_M $LiPF_6$ or 1_M LiBOB in a mixture of ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 v/v; PANAX ETEC Co. Ltd, Korea), $LiMn_2O_4$ (Nikki Chemical Co., Ltd., Japan, w/o surface treatment), Super-P conductive carbon black (C65, TIMCAL), *N*-methyl-2-pyrrolidone (NMP, Aldrich), graphite (Mitsubishi Chem. Co., Japan, w/o surface treatment) were used without further purification. Lithium metal (0.1 mm) was purchased from Honzo, Japan. Microporous films of polyethylene (Asahi Kasei, thickness: 25 µm, porosity: 40%) were used as separators.

2. Preparation for ^{13}C-NMR characterization

For high resolution NMR spectra, the molecular weight of the alginate was reduced by a partial hydrolysis step following the procedure described by N. Emmerichs *et al.*[S2] Alginate (200 mg) was dissolved in 20 mL of distilled water. Hydrochloric acid (1 N) was added to the alginate solution until the pH value was less than 3.0, and the solution was then stirred gently at 100 ˚C for 1 h. After the hydrolysis, the solution was cooled down and neutralized with sodium hydroxide (1N). The neutralized solution was dialyzed overnight with distilled water and lyophilized.

3. ^{13}C-NMR results for the alginate binder

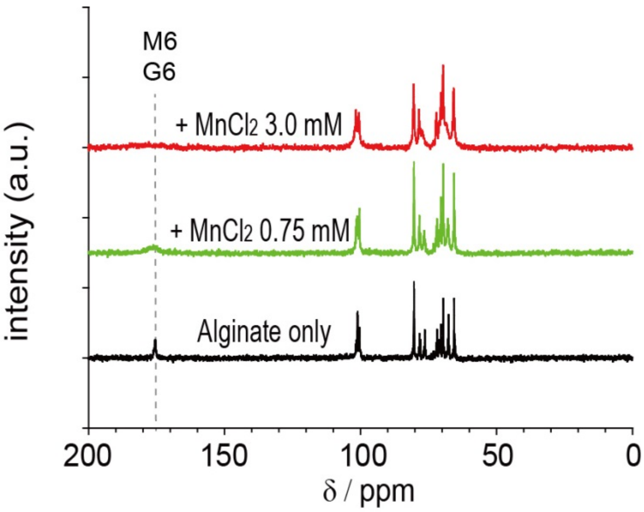

Figure S1. ^{13}C-NMR spectra of alginate at various $MnCl_2$ concentrations measured in the δ range of 200 - 0 ppm.

4. Polymer film preparation

Polymer solutions (Alginate: 5 wt% in distilled water, PVDF: 10 wt% in acetone) were cast on glass substrates by the doctor blade technique for generation of 150 μm thick films. Next, the cast films were immersed in nonsolvents (acetone for alginate and DI water for PVDF). Solidification of the cast polymers was performed by simultaneous solvent-nonsolvent exchange and subsequent solvent evaporation.

5. Electrochemical measurements

LMO/Li metal half-cells were precycled between 3.0 and 4.5 V vs. Li/Li^+ under constant current mode at C/10 (0.04 mA cm^{-2}, both charging and discharging processes) at 25 ˚C, and then cycled at 1C (0.4 mA cm^{-2}, constant current-constant voltage mode in charging process and constant current mode in discharging process) at 25 or 55 ˚C.

LMO/graphite full-cells were precycled between 3.0 and 4.2 V at C/10 (0.035 mA cm^{-2}, constant current mode in both charging and discharging processes) at 25 ˚C, and then cycled at 1C (0.35 mA cm^{-2}, constant current-constant voltage mode in charging processes and constant current mode in discharging processes) at 25 ˚C or 55 ˚C.

6. Summary of capacity retention data

Table S1. List of capacity retention data achieved with the $LiPF_6$ electrolyte.

Binder	Lithium salt	Types	T [°C][a]	Cycles	Retention [%][b]
Alginate	$LiPF_6$	Half	25	120	97.7
PVDF	$LiPF_6$	Half	25	120	82.5
Alginate	$LiPF_6$	Half	55	120	94.9
-	-	-	-	250	90.3
PVDF	$LiPF_6$	Half	55	120	77.6
-	-	-	-	250	73.2
Alginate	$LiPF_6$	Full	25	400	54.0
PVDF	$LiPF_6$	Full	25	400	32.8
Alginate	$LiPF_6$	Full	55	100	37.7
PVDF	$LiPF_6$	Full	55	100	20.1

[a] Operation temperature.

[b] (discharge capacity / initial discharge capacity) × 100

Table S2. List of capacity retention data achieved with the LiBOB electrolyte.

Binder	Lithium salt	Types	T [˚C][a]	Cycles	Retention [%][b]
Alginate	LiBOB	Half	25	220	96.3
PVDF	LiBOB	Half	25	220	94.2
Alginate	LiBOB	Half	55	100	92.7
PVDF	LiBOB	Half	55	100	91.2
Alginate	LiBOB	Full	25	200	79.4
PVDF	LiBOB	Full	25	200	76.4
Alginate	LiBOB	Full	55	110	64.6
PVDF	LiBOB	Full	55	110	51.7

[a] Operation temperature.

[b] (discharge capacity / initial discharge capacity) × 100

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A
This journal is © The Royal Society of Chemistry 2013

7. Charge-discharge potential profiles: $LiPF_6$ based electrolytes

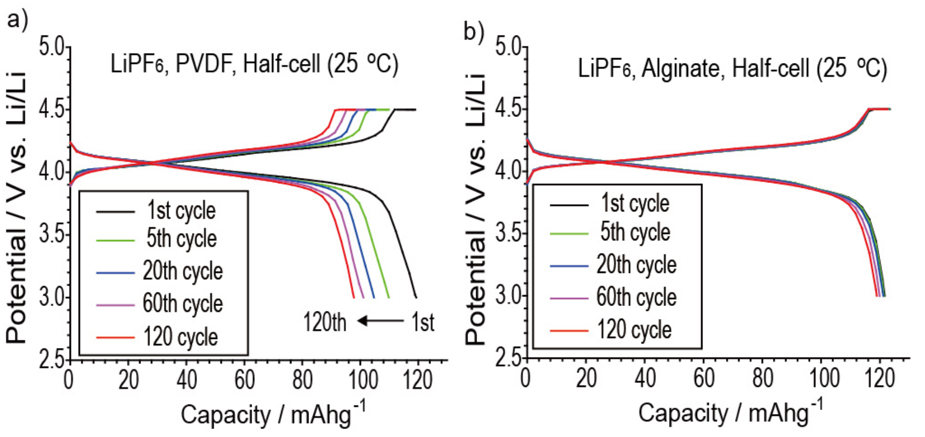

Figure S2. Charge-discharge potential profiles of LMO/Li metal half-cells based on $LiPF_6$ electrolyte. The corresponding capacity retentions are shown in Figure 2b (25 ˚C, 1C-rate).

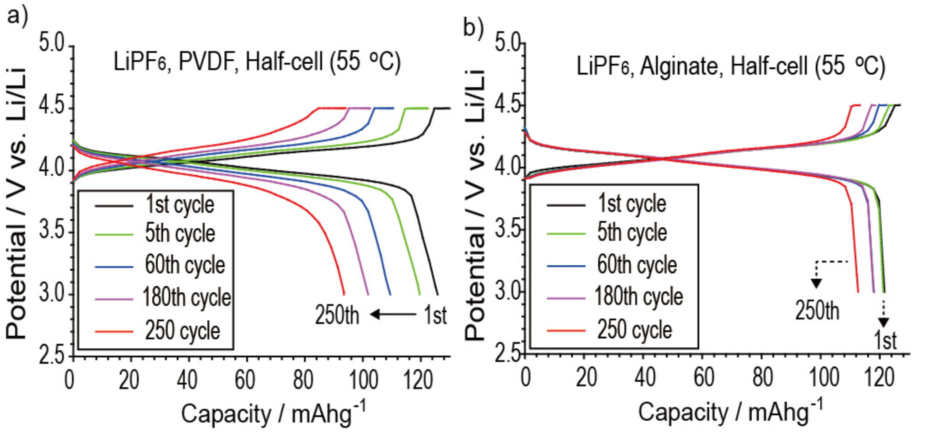

Figure S3. Charge-discharge potential profiles of LMO/Li metal half-cells based on $LiPF_6$ electrolyte. The corresponding capacity retentions are shown in Figure 2c (55 ˚C, 1C-rate).

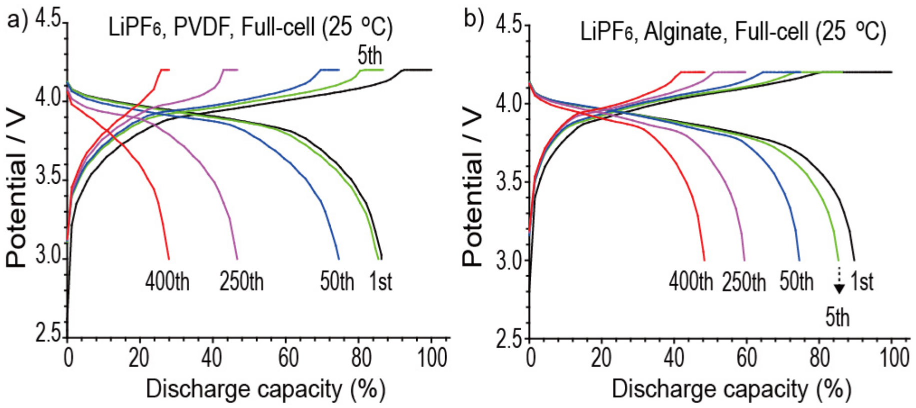

Figure S4. Charge-discharge potential profiles of LMO/graphite full-cells based on $LiPF_6$ electrolyte plotted. The corresponding capacity retentions are shown in Figure 2d (25 ˚C, 1C-rate).

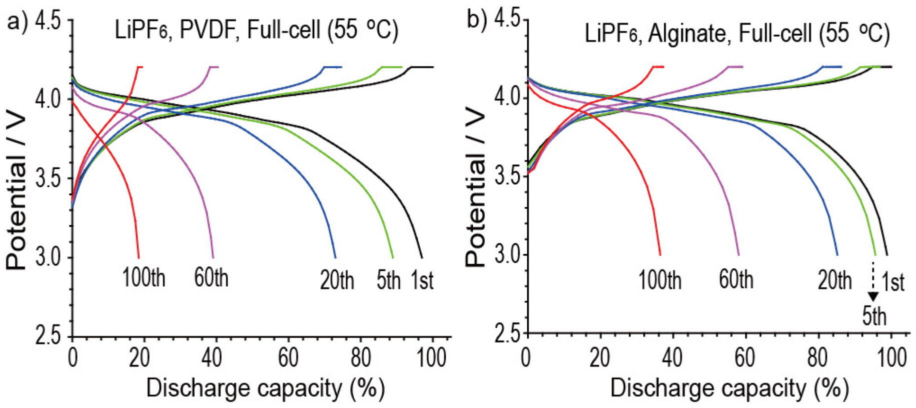

Figure S5. Charge-discharge potential profiles of LMO/graphite full-cells based on $LiPF_6$ electrolyte. The corresponding capacity retentions are shown in Figure 2e (55 ˚C, 1C-rate).

8. Charge-discharge potential profiles: LiBOB based electrolytes

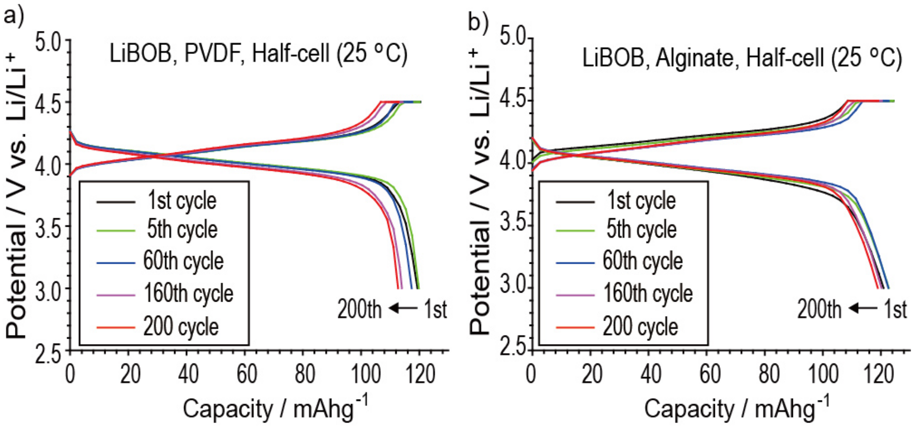

Figure S6. Charge-discharge potential profiles of LMO/Li metal hall-cells based on LiBOB electrolyte. The corresponding capacity retentions are shown in Figure 3b (25 ˚C, 1C-rate).

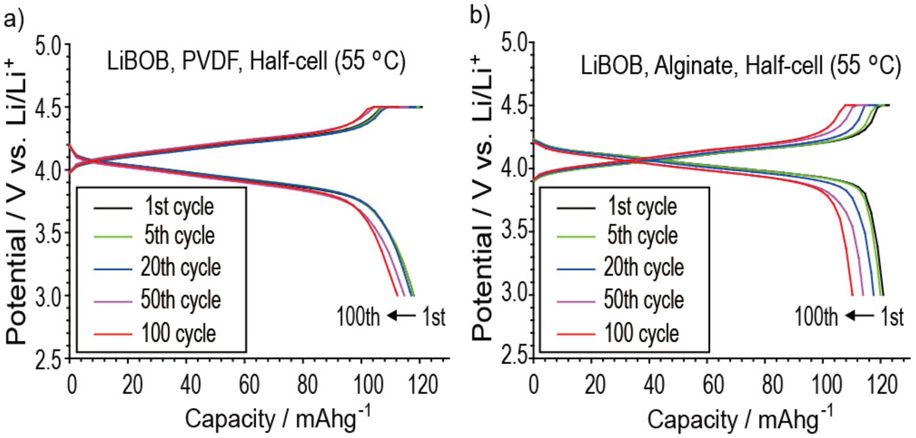

Figure S7. Charge-discharge potential profiles of LMO/Li metal hall-cells based on LiBOB electrolyte. The corresponding capacity retentions are shown in Figure 3c (55 ˚C, 1C-rate).

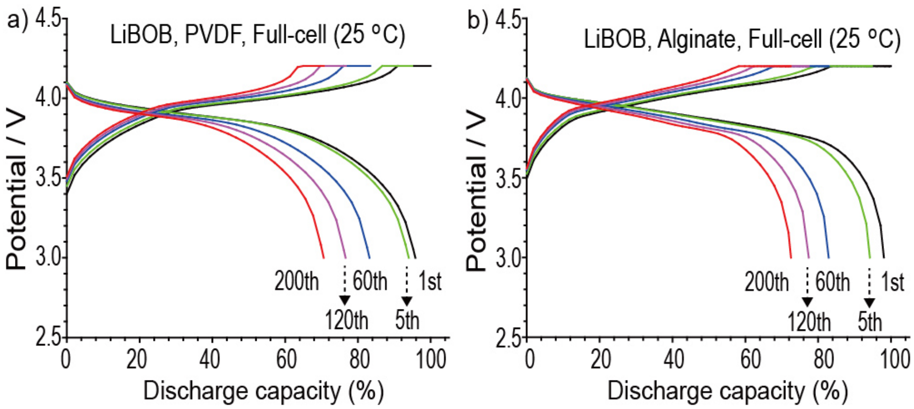

Figure S8. Charge-discharge potential profiles of LMO/graphite full-cells based on LiBOB electrolyte. The corresponding capacity retentions are shown in Figure 3d (25 ˚C, 1C-rate).

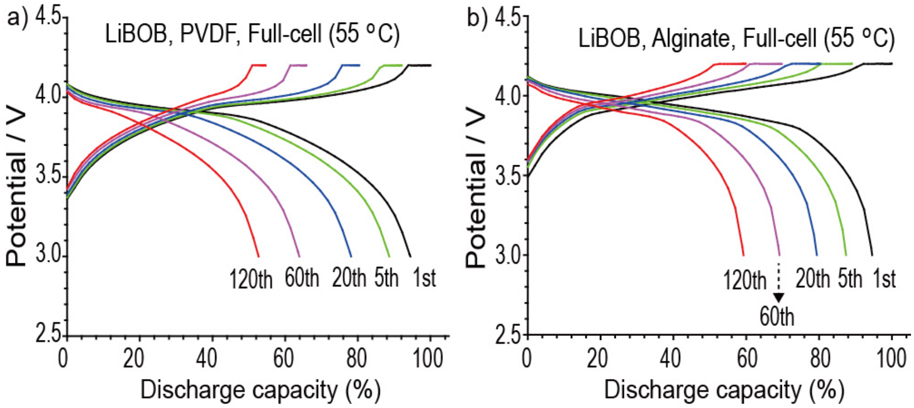

Figure S9. Charge-discharge potential profiles of LMO/graphite full-cells based on LiBOB electrolyte. The corresponding capacity retentions are shown in Figure 3e (55 ˚C, 1C-rate).

9. Electrochemical stabilities of polymeric binders

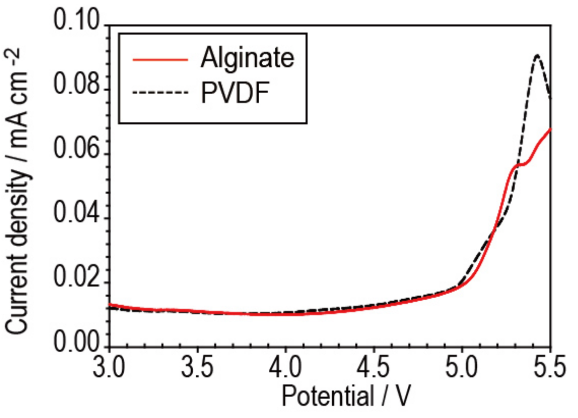

Figure S10. LSV data of binder/super-P composite electrodes (Li metal/separator/composite on stainless steel plate, binder: super-P = 80:20 by weight, 0 – 5.5 V vs. Li/Li^+ with a scan rate 1.0 mV s^{-1}). A mixture of EC:DEC=1:1 by vol. containing 1_M $LiPF_6$ was used as liquid electrolyte.

10. The protective effect of alginate on the dissolution of spinel $LiMn_2O_4$ in the electrolyte

We monitored the concentration of dissolved Mn ions in the electrolyte after immersion of LMO with the PVdF and Alginate binders in the electrolyte for 5 days at 25 and 55 °C.

Table S3. Mn concentration in the electrolyte after the storage tests at 25 °C.

25 °C storage	Only $LiMn_2O_4$	$LiMn_2O_4$ with Alginate binders	$LiMn_2O_4$ with PVdF binders
Mn concentration / ppm	4.01	2.26	3.85

Table S4. Mn concentration in the electrolyte after the storage tests at 55 °C.

55 °C storage	Only $LiMn_2O_4$	$LiMn_2O_4$ with Alginate binders	$LiMn_2O_4$ with PVdF binders
Mn concentration /ppm	469	318.8	458

[S1] M.-H. Ryou, J. Kim, I. Lee, S. Kim, Y. K. Jeong, S. Hong, J. H. Ryu, T.-S. Kim, J.-K. Park, H. Lee, J. W. Choi, *Adv. Mater.* **2013**, *11*, 1571.

[S2] N. Emmerichs, J. Wingender, H.-C. Flemming, C. Mayer, *Int. J. Bio. Macromol.* **2004**, *34*, 73.