Supplementary information

Lithium-selective hybrid capacitive deionization system with Ag-coated carbon electrode and stop-flow operation

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Hongsik Yoon *[,1], Taijin Min [1], Jiho Lee [2], Gunhee Lee [1], Minkyu Jeon [1], Areum Kim [3]

[1] Department of Sustainable Environment Research, Korea Institute of Machinery & Materials, Daejeon 34103, Republic of Korea

[2] Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, IL 61801, United States

[3] Department of Nano-Mechanics, Korea Institute of Machinery & Materials, Daejeon 34103, Republic of Korea

[*] Corresponding author: Hongsik Yoon, Email: yoonhs@kimm.re.kr, Phone: +82-42-868-7891

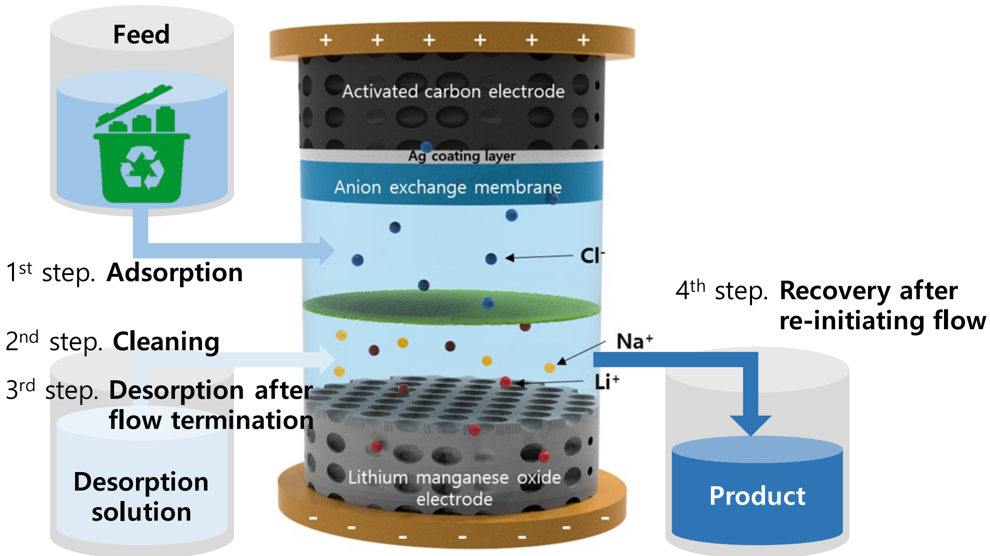


Fig. S1 Schematics of the stop-flow operation procedure.

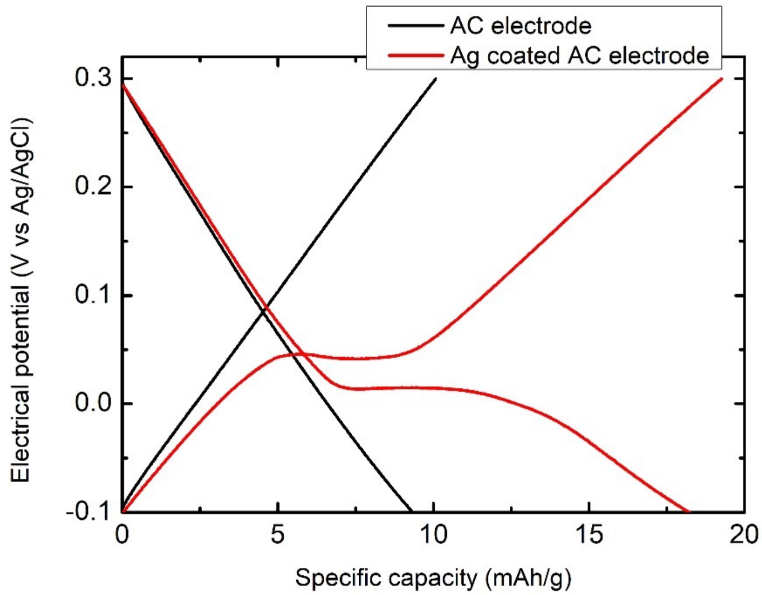
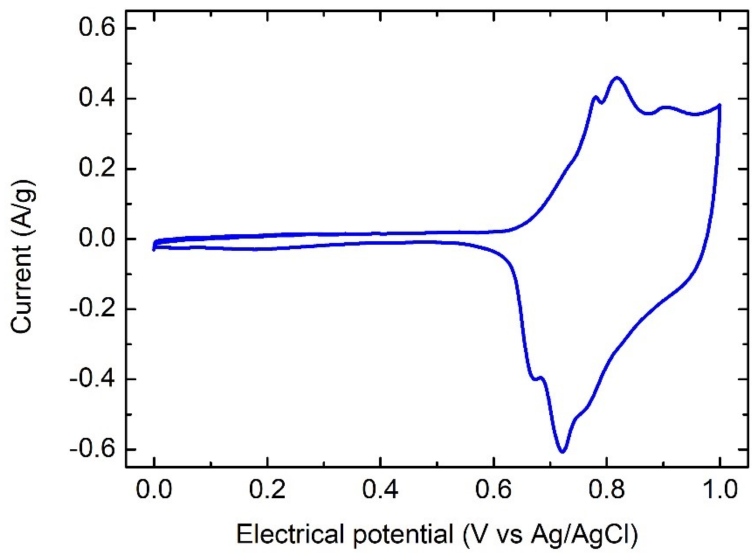


Fig. S2 Galvanostatic charging/discharging profile of the activated carbon (AC) electrode and Ag coated AC electrode (Current density: 0.5 mA/cm2, Cut-voltage: 0.3 V / -0.1 V, Electrolyte: 2 M $LiCl_2$)



(b)

Fig. S3 Cyclic voltammetry profiles of lithium manganese oxide electrode (Electrolyte: 2 M LiCl; Scan rate: 1 mV/s; Reference electrode: Ag/AgCl KCl sat'd).

Table S1 Li^+ recovery capacity per unit energy consumption of lithium recovery system according to the counter electrode (AC: Activated carbon, Ag: Silver, Zn: Zinc, PANI: Polyaniline, NiHCF: Nickel Hexacyanoferrate)

Counter electrode	Operation mode (Current density)	Solution compositio n	Li^+ recovery capacity / Energy consumption (mol_{Li}/Wh)	Reference
Ag coated AC electrode	**CC mode (0.5 mA/cm²)**	**Li^+ 10 mM**	**0.34**	**This study**
Ag	CC mode (0.5 mA/cm²)	Li^+ 210 mM	1.0	[1]
AC	CC mode (0.5 mA/cm²)	Li^+ 30 mM (LiCl, NaCl, KCl, $MgCl_2$, and $CaCl_2$)	0.24	[2]
Zn	CC mode (0.5 mA/cm²)	Li^+ 210 mM	0.16	[3]
PANI	CC mode (0.5 mA/cm²)	Li^+ 64 mM	0.25	[4]
NiHCF	CC mode (1 C)	Li^+ 42 mM	0.28	[5]

Table R1 provides the Li^+ recovery capacity per unit energy consumption from the result in Fig 2 and Eq. (5) and from previous studies. It is noted that comparisons were made with literature values evaluated under similar current density conditions. As shown in Table R1, Li^+ recovery capacity per unit energy consumption of this system (HCDI with Ag coated AC electrode) showed 0.34 mol_{Li}/Wh, which was better than the values reported in the literature, except the system using the Ag electrode. On the other hand, 1.0 mol_{Li}/Wh was reported for the Li recovery system with Ag electrode as counter electrode.[1] Therefore, a lithium recovery system with Ag counter electrode is more advantageous in aspect of lithium recovery capacity per unit energy consumption than HCDI with Ag coated AC electrode.

However, Ag is a precious and expensive metal. It appears that a significant cost is expected (estimated at 222 - 300 USD/m²) considering the amount and price of Ag in the

Ag electrode (30 – 40 mg/cm^2).[1,6] On the other hand, only 4 – 5.3% of Ag is required for Ag coating in this study (estimated at 1.2 USD/m^2).[6] Therefore, since the Ag electrode and the Ag coated AC electrode have clearly different advantages in terms of energy consumption and Ag cost, they could be used selectively according to the user's priority.

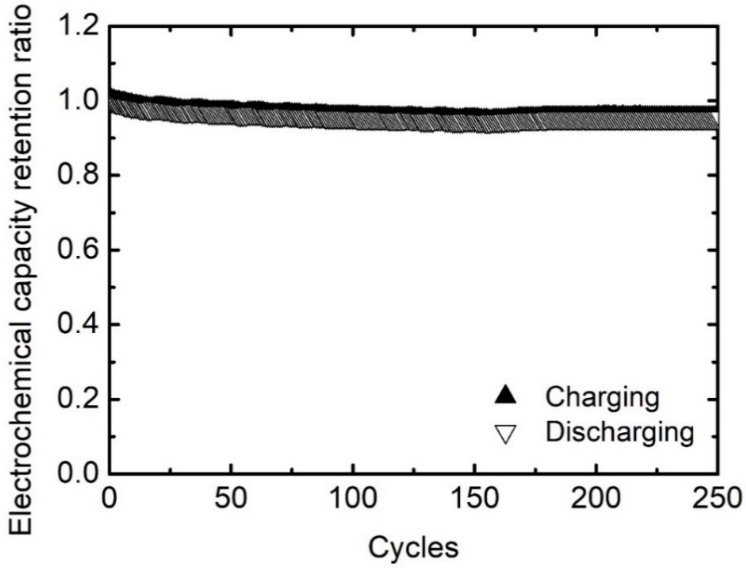


Fig. S4 Electrochemical capacity retention ratio of Li-selective hybrid capacitive deionization system (Negative electrode: lithium manganese oxide electrode; Positive electrode: Ag-coated activated carbon electrode; Current: 10 mA/cm^2; Voltage cut-off: 1.0 V/-1.0 V)

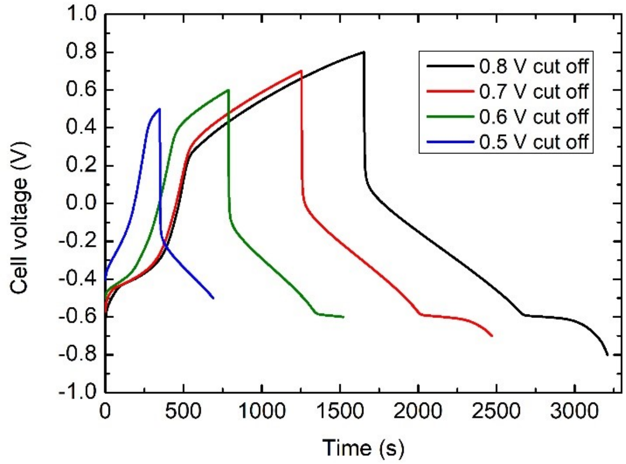


Fig. S5 Cell voltage profile with cut-off voltage (Feed: 10 mM LiCl; Negative electrode: lithium manganese oxide electrode; Positive electrode: activated carbon (AC) electrode or Ag-coated AC electrode; Cut-off voltage: 0.5–0.8 V; Current: 0.5 mA/cm^2 at adsorption/-0.5 mA/cm^2 at desorption; Flow rate: 2 mL/min)

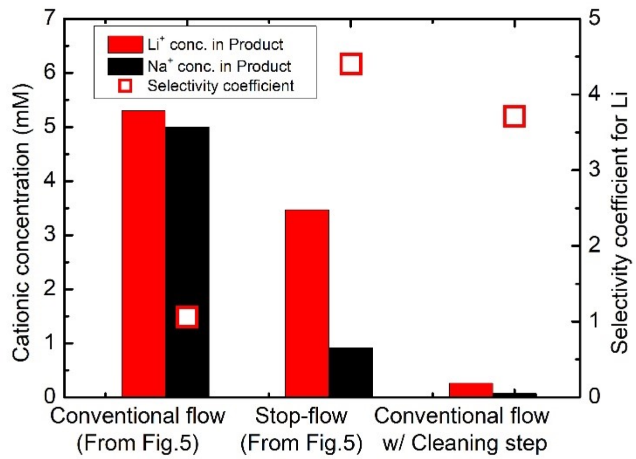


Fig. S6 Cationic concentration in the product solution and Li^{+} selectivity coefficient in the Li-selective hybrid capacitive deionization system under conventional flow (From Fig. 5), stop-flow (From Fig. 5) and conventional flow with cleaning step (Negative electrode: lithium manganese oxide electrode; Positive electrode: Ag-coated activated carbon electrode; Feed: 5 mM LiCl + 5 mM NaCl; Current: 0.5 mA/cm2; Voltage cut-off: 1.0 V/-1.0 V; Flow rate: 2 mL/min).

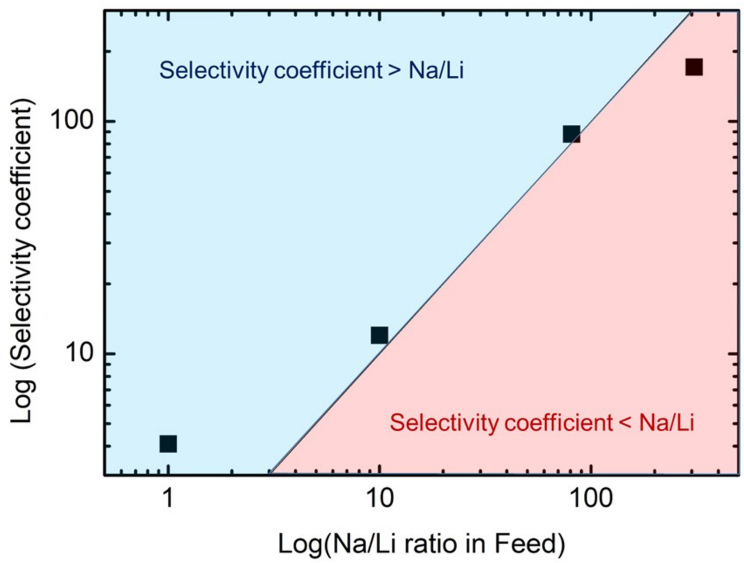


Fig. S7 Selectivity coefficient with Na/Li ratio in feed solution of the Li-selective hybrid capacitive deionization system with LMO/Ag-coated AC electrode configuration. Blue section: selectivity coefficient > Na/Li ratio, Red section: selectivity coefficient < Na/Li ratio. LMO: lithium manganese oxide; AC: activated carbon.

References

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6 IMF primary commodity price database, https://www.imf.org/en/Research/commodity-prices, (accessed October 2022).