Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Low-cost batteries based on industrial waste Al-Si microparticles and $LiFePO_4$ for stationary energy storage

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Supplementary Note

1. Discussion of chemical stability of $LiPF_6$ ether electrolytes

Although ether-based electrolytes showed promising prospects for alloy anodes, not all ethers are adaptable with the most common salt, $LiPF_6$. Only several ethers with a specific structure exhibit good compatibility with $LiPF_6$. We studied the physical state changes of various commonly used ethers solvents containing 1.0 M $LiPF_6$ along with time, including THF, 2-MeTHF, THF/2-MeTHF (THF: 2-MeTHF = 1:1, vol.), dimethoxyethane (DME), 1,3-dioxolane (DOL). At the very beginning of adding 1.0 M $LiPF_6$ to the mentioned five ether solvents and baseline EC/DMC solvent, colorless (or slightly yellow) and transparent solutions were acquired for all the above solvents. After only 5 minutes, a violent reaction accompanied by heat generation was observed in DOL solvent, and the overall solution transformed to gelatinous soon. The reaction of $LiPF_6$ with $LiPF_6$ and DME occurred soon after and lasted for several days. Eventually, the whole solution of THF electrolyte and ~1/3 of DME electrolyte converted to gelatinous. There are no noticeable state changes in 2-MeTHF, THF/2-MeTHF, and EC/DMC solutions after one month.

2. Discussion of chemical stability of $LiPF_6$ ether electrolytes

We compared the solvation structure information from the Raman band shift of the PF_6^- anion in various electrolytes. As Fig. S15 shows, an increased Raman peak blueshift of the ~741 cm^{-1} band[1] assigned to PF_6^- was observed in the sequence of 1.0 M $LiPF_6$ EC/DMC < 1.0 M $LiPF_6$ 2-MeTHF < 2.0 M $LiPF_6$ 2-MeTHF, which suggests the rising ionic association between PF_6^- and Li^+. The strong $PF_6^-\cdots Li^+$ binding energy in 2-MeTHF-based electrolytes leads to the formation of contact ion pairs (CIPs) and aggregates (AGGs).[2, 3] In addition, the blueshift of CH_2 stretch Raman shift showed a decrease in the following order: 1.0 M $LiPF_6$ EC/DMC > 2.0 M $LiPF_6$ 2-MeTHF > 1.0

M $LiPF_6$ 2-MeTHF, which means the reduced solvation ability in 2-MeTHF-based electrolytes. The combination of these two factors renders an elevated LiPF6 reduction potential much prior to the ether solvent,[4] facilitating the formation of LiF and suppressing the decomposition of the solvent. We finally chose to use 2.0 M $LiPF_6$ 2-MeTHF for the subsequent tests based on the above analysis.

Supplementary Figure

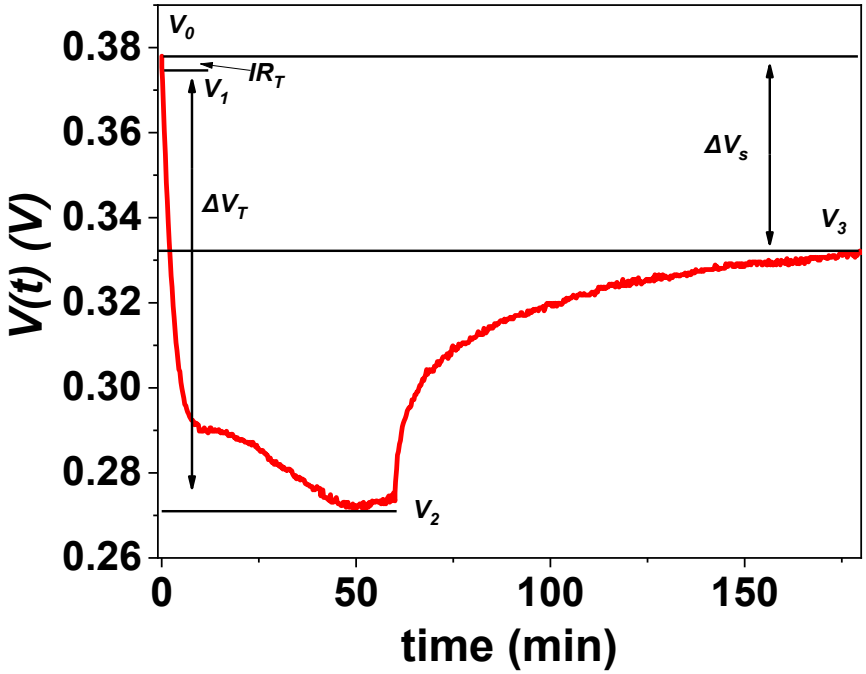

Fig. S1 A typical magnified voltage-time profile of one discharge pulse derived from GITT.

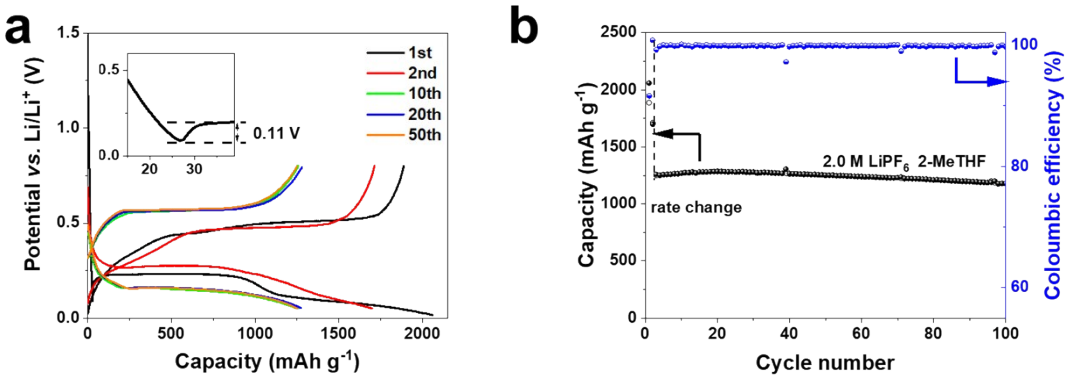

Fig. S2 a) Typical charge/discharge profiles and **b)** Cycling stability and CE of Al-SiMP electrode cycled in 2.0 M $LiPF_6$ 2-MeTHF. The rates were C/10 at the initial 2 cycles and 2C at the subsequent cycles.

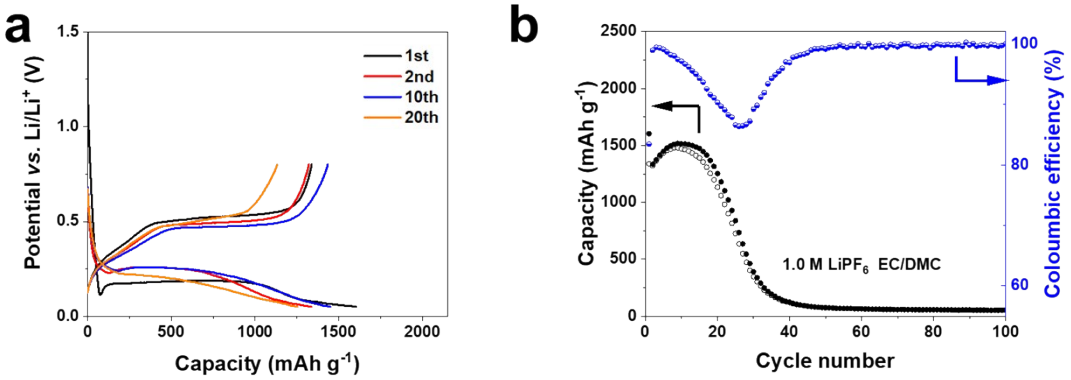

Fig. S3 a) Typical charge/discharge profiles and **b)** Cycling stability and CE of Al-SiMP electrode cycled in 1.0 M $LiPF_6$ EC/DMC. The rate was C/10.

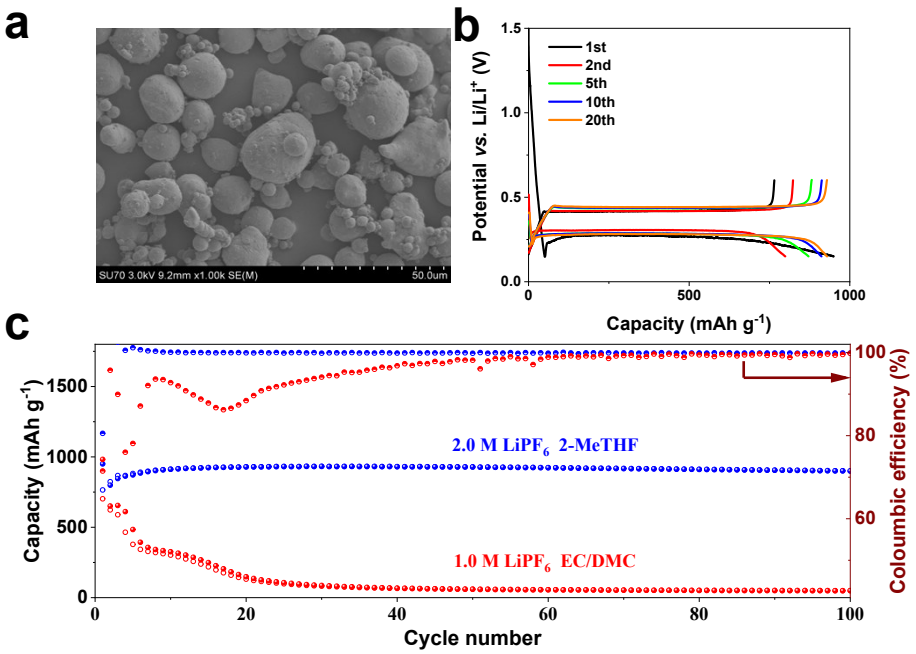

Fig. S4 a) SEM images of AlMPs. **b)** Voltage profiles of AlMPs cycled in 2.0 M $LiPF_6$ 2-MeTHF electrolyte. **c)** Cycling performance and CEs of AlMPs cycled in 2.0 M $LiPF_6$ 2-MeTHF electrolyte.

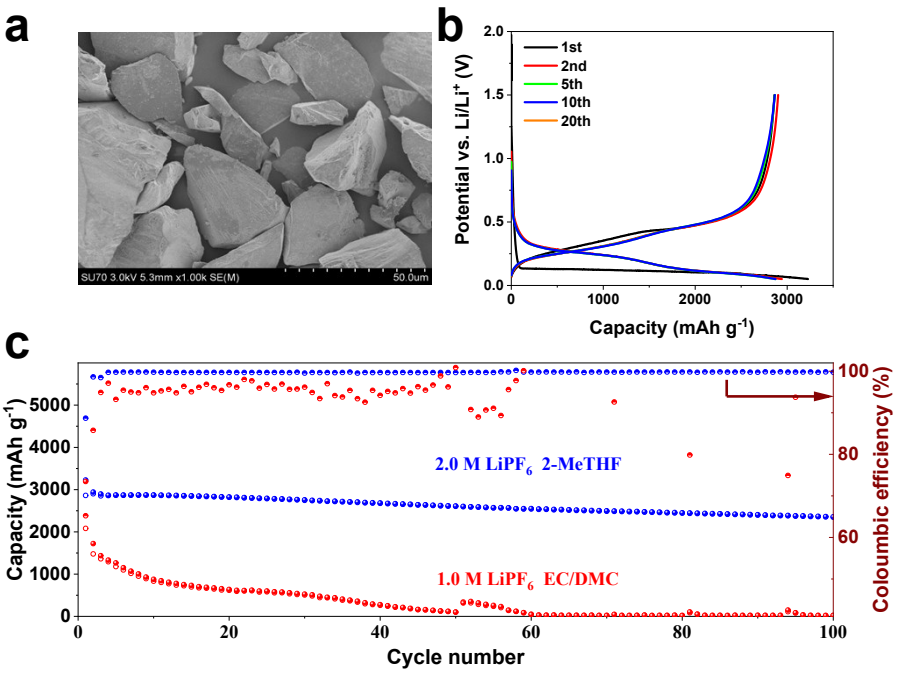

Fig. S5 a) SEM images of SiMPs. **b)** Voltage profiles of SiMPs cycled in 2.0 M $LiPF_6$ 2-MeTHF electrolyte. **c)** Cycling performance and CEs of SiMPs cycled in 2.0 M $LiPF_6$ 2-MeTHF electrolyte.

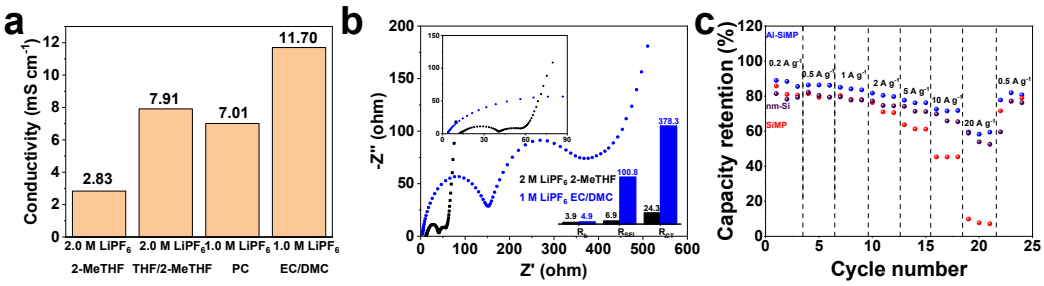

Fig. S6 a) Ionic conductivity comparison of various electrolytes. **b)** EIS in Nyquist plots of Al-SiMPs in 2.0 M $LiPF_6$ 2-MeTHF electrolyte (black), 1.0 M $LiPF_6$/EC-DMC electrolyte (blue). **c)** The comparison of rate performance of Al-SiMP (blue), nano-Si (purple), and SiMP (red).

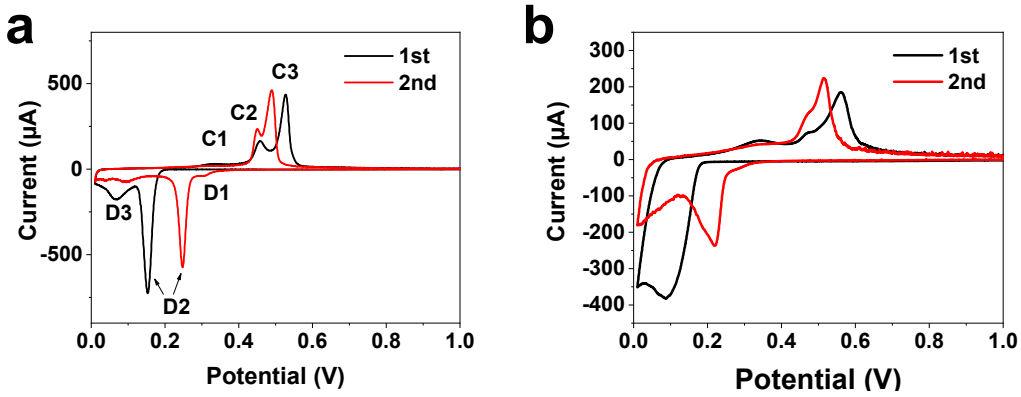

Fig. S7 CV curves of Al-SiMPs cycled in **a)** 2.0 M $LiPF_6$ 2-MeTHF and **b)** 1.0 M $LiPF_6$/EC-DMC electrolyte.

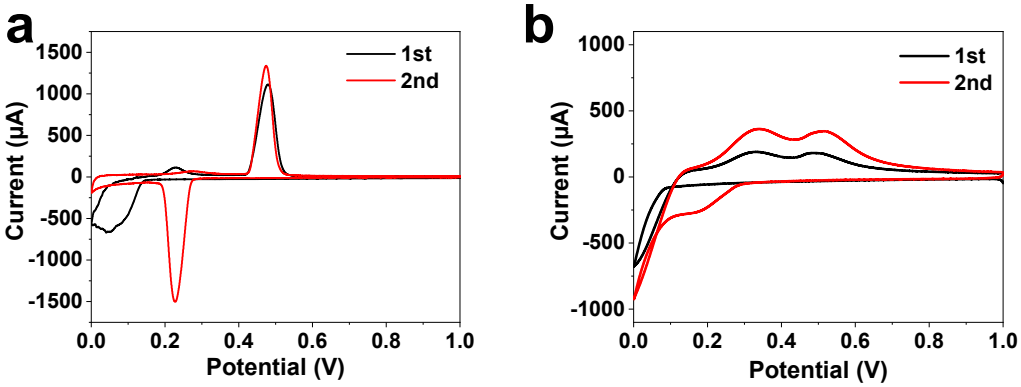

Fig. S8 CV curves of **a)** AlMPs, **b)** SiMPs cycled in 2.0 M $LiPF_6$ 2-MeTHF.

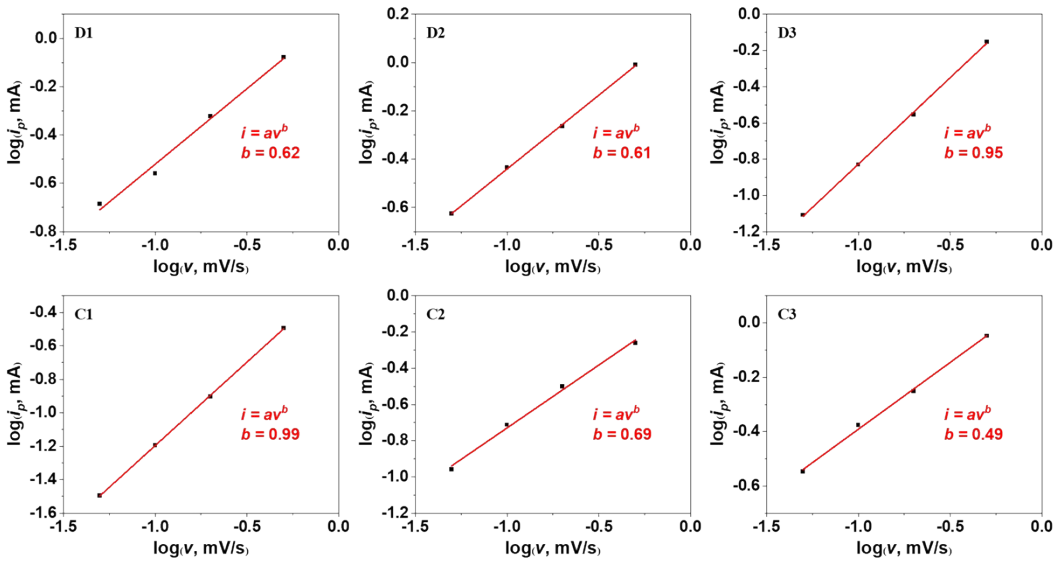

Fig. S9 Log *i* (peak current) *vs.* log *v* (scan rate) plots at charging/discharging from the CV curves of Al-SiMPs.

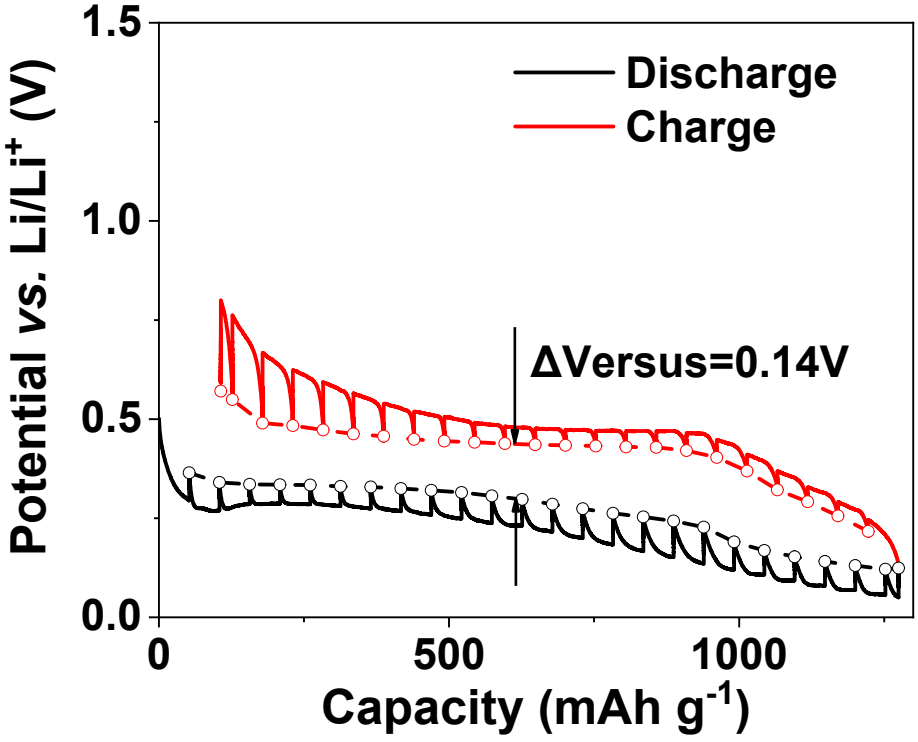

Fig. S10 GITT profiles of Al-SiMPs in 1.0 M $LiPF_6$ EC/DMC.

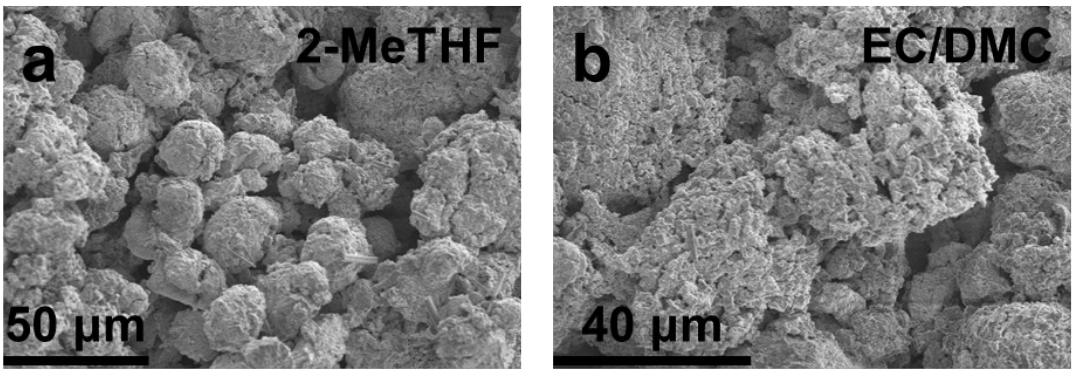

Fig. S11 SEM images of **a)** Al-SiMPs cycled in 2.0 M $LiPF_6$ 2-MeTHF electrolyte after 5 cycles, and **b)** Al-SiMPs cycled in 1.0 M $LiPF_6$ EC/DMC electrolyte after 5 cycles.

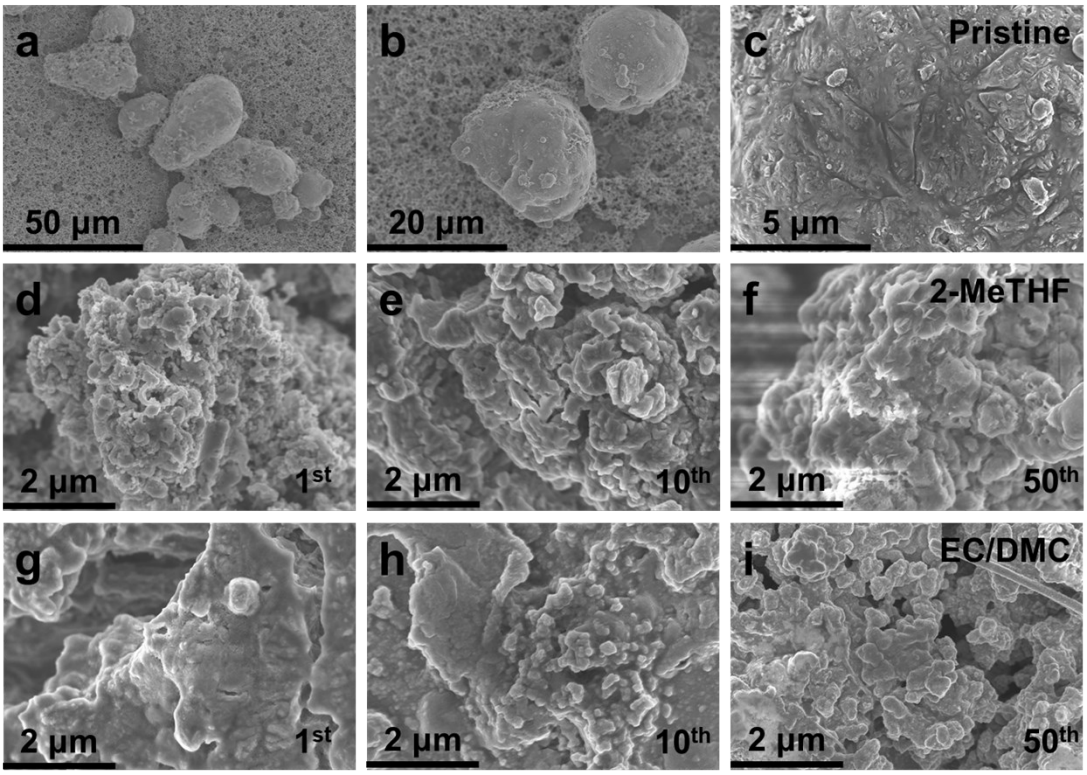

Fig. S12 SEM images of **a)**, **b) c)** pristine Al-SiMPs. **d)**, **e), f)** Al-SiMPs cycled in 2.0 M $LiPF_6$ 2-MeTHF electrolyte after 1, 10, 50 cycles. **g)**, **h), i)** Al-SiMPs cycled in 1.0 M $LiPF_6$/EC-DMC electrolyte after 1, 10, 50 cycles.

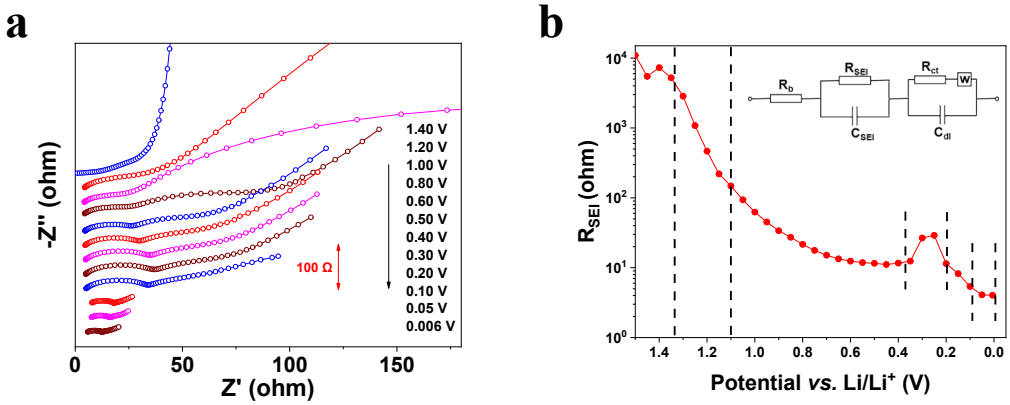

Fig. S13 a) EIS of Al-Si electrode in the 2-MeTHF-based electrolyte at various potentials recorded during the first lithiation process: from 1.4 V to 0.006 V. **b)** Potential dependences of R_{SEI} of the Al-Si anode in the 2-MeTHF-based electrolyte.

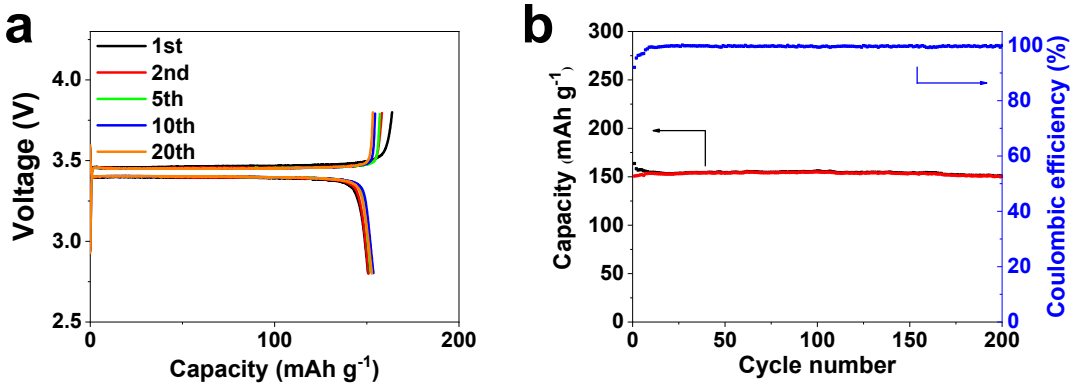

Fig. S14 a) Voltage profiles and **b)** cycling performance of LFP cathode cycled in 2.0 M $LiPF_6$ 2-MeTHF electrolyte.

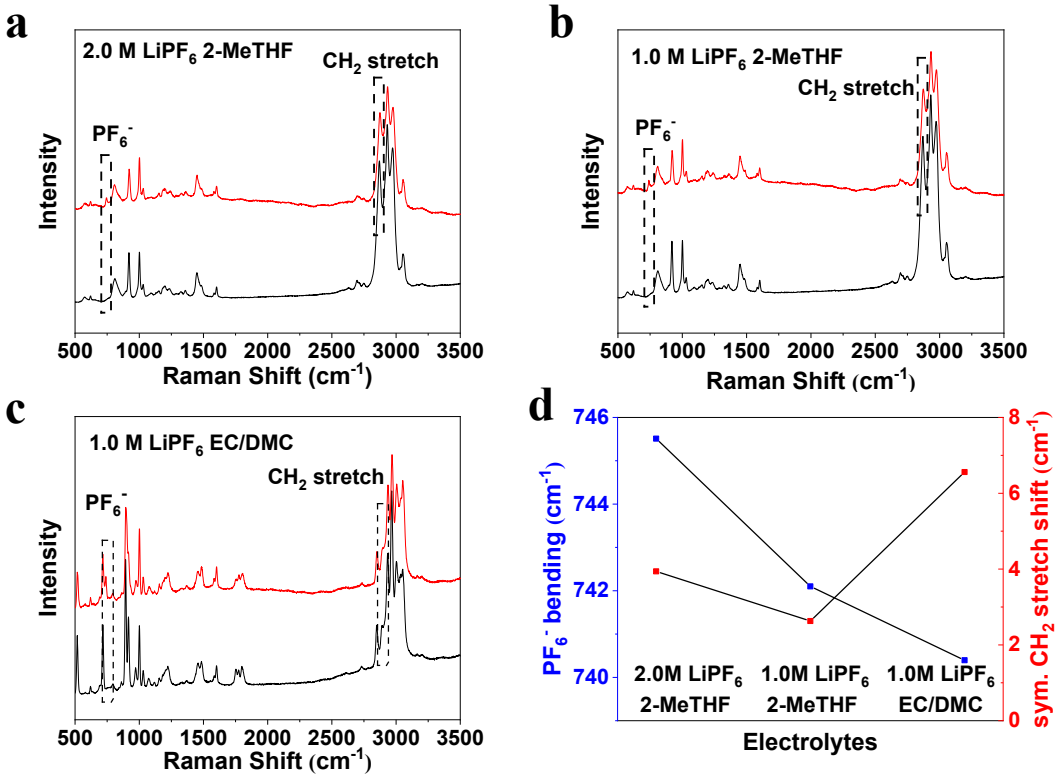

Fig. S15 Raman spectra of various electrolytes with their pure solvent: a) 2.0 M $LiPF_6$ 2-MeTHF, b) 1.0 M $LiPF_6$ 2-MeTHF, c) 1.0 M $LiPF_6$ EC/DMC. d) The peak shift trend of PF_6^- and CH_2 stretch.

Reference

[1] C.M. Burba, R. Frech, *J. Phys. Chem. B,* 2005, **109,** 15161-15164.

[2] J. Ming, Z. Cao, W. Wahyudi, M.L. Li, P. Kumar, Y.Q. Wu, J.Y. Hwang, M.N. Hedhili, L. Cavallo, Y.K. Sun, L.J. Li, *Acs Energy Lett.* 2018, **3,** 335-340.

[3] Y. Yamada, K. Furukawa, K. Sodeyama, K. Kikuchi, M. Yaegashi, Y. Tateyama, A. Yamada, *J. Am. Chem. Soc.* 2014, **136,** 5039-46.

[4] J. Chen, X. Fan, Q. Li, H. Yang, M.R. Khoshi, Y. Xu, S. Hwang, L. Chen, X. Ji, C. Yang, H. He, C. Wang, E. Garfunkel, D. Su, O. Borodin, C. Wang, *Nat. Energy* 2020, **5,** 386-397.