Electronic Supplementary Information (ESI)

Solid solution phosphide ($Mn_{1-x}Fe_xP$) as a tunable conversion/alloying hybrid anode for lithium-ion batteries

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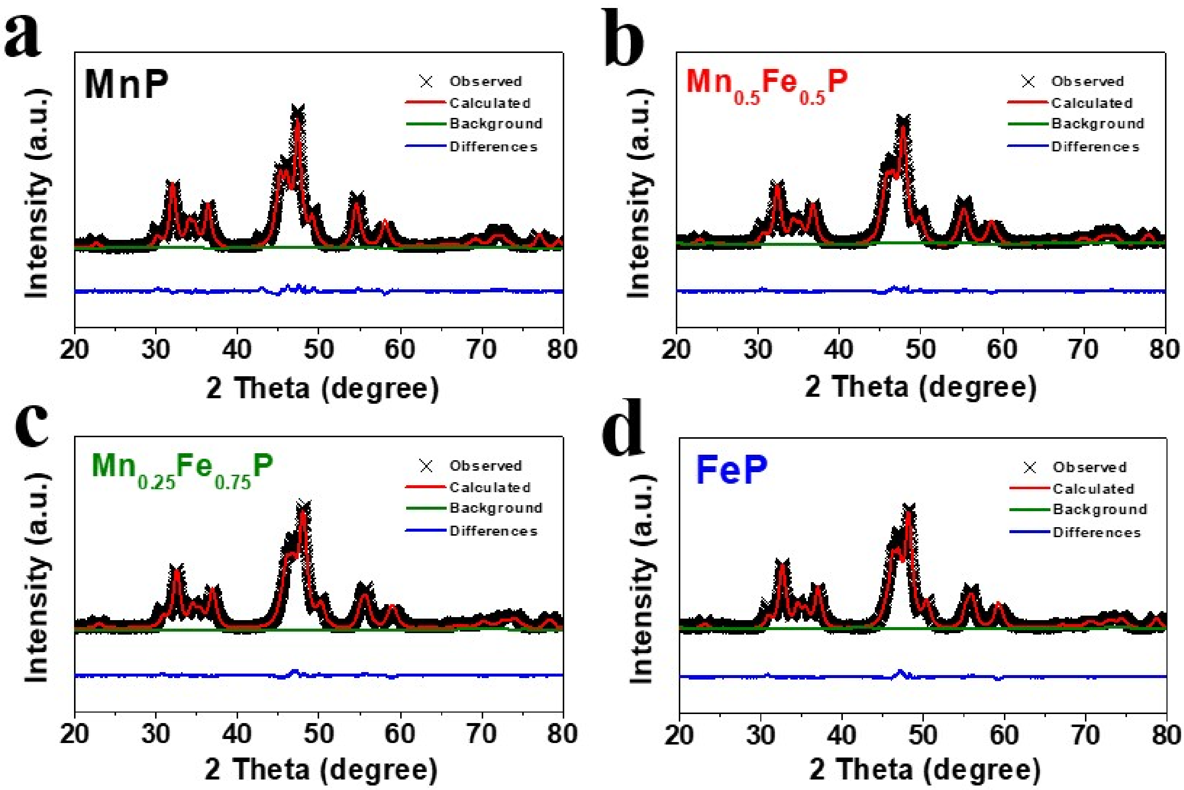

Fig. S1 XRD Rietveld refinement results for as-synthesized $Mn_{1-x}Fe_xP$ (x = 0, 0.5, 0.75, and 1.0) NPs.

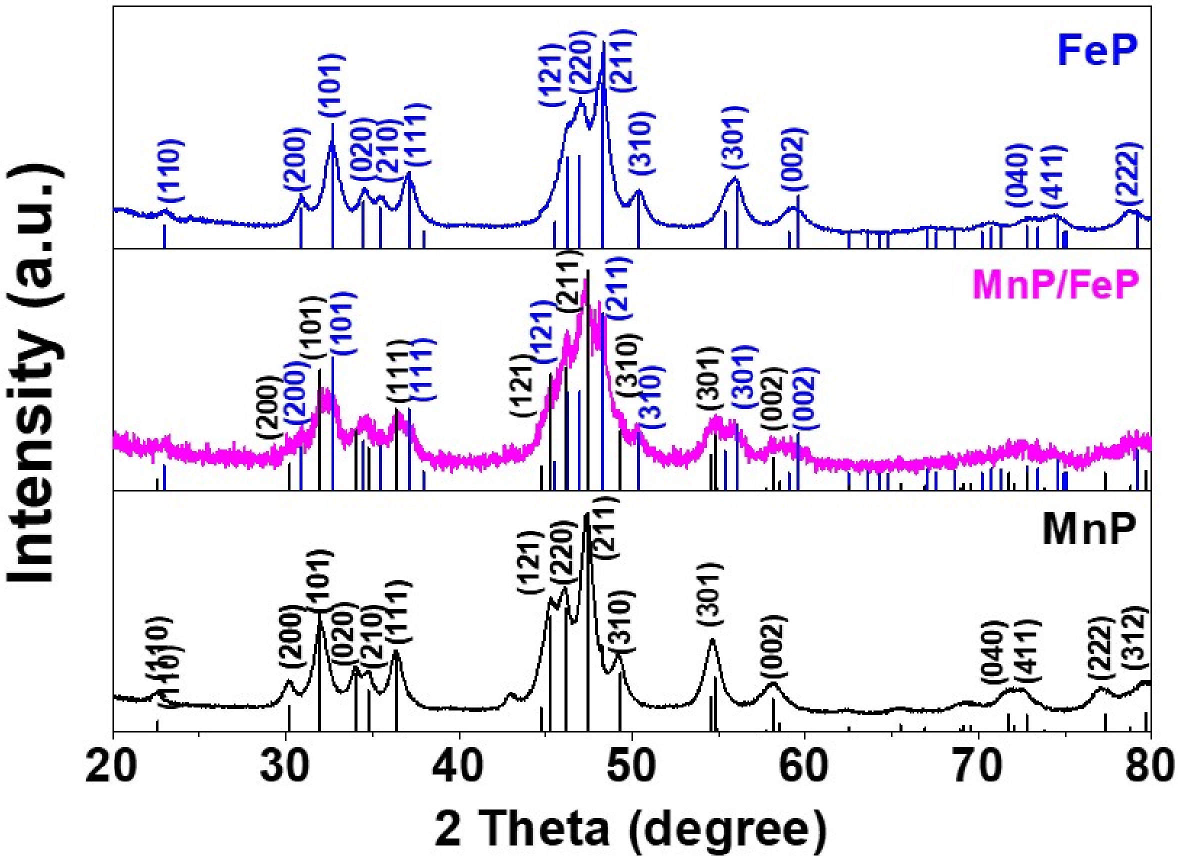

Fig. S2 XRD patterns of as-synthesized MnP, MnP/FeP mixture, and FeP NPs. The reference peaks for MnP (ICDD # 00-051-0942, black color) and FeP (ICDD # 01-078-1443, blue color) are included.

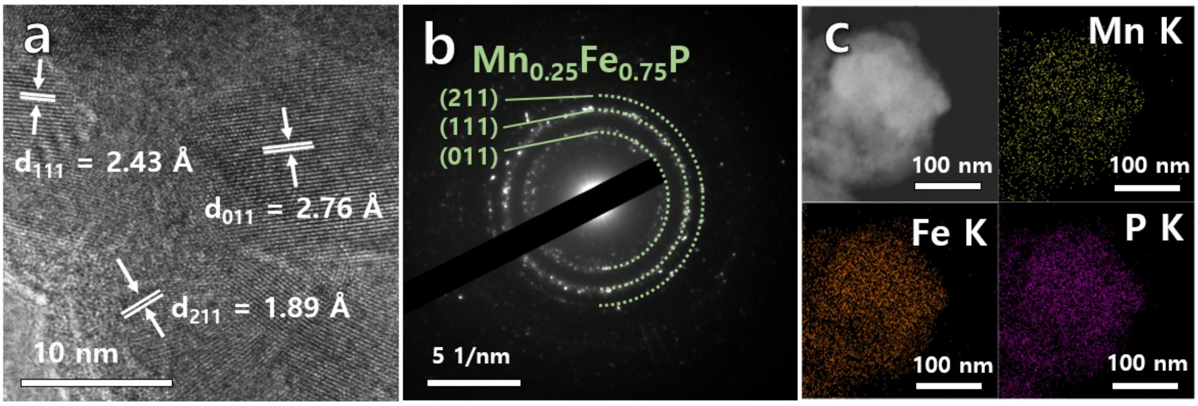

Fig. S3 (a) HRTEM image, (b) SAED pattern, and (c) STEM and EDS element mapping images (Mn K, Fe K, and P K) of as-prepared $Mn_{1-x}Fe_xP$ (x = 0.75) NPs.

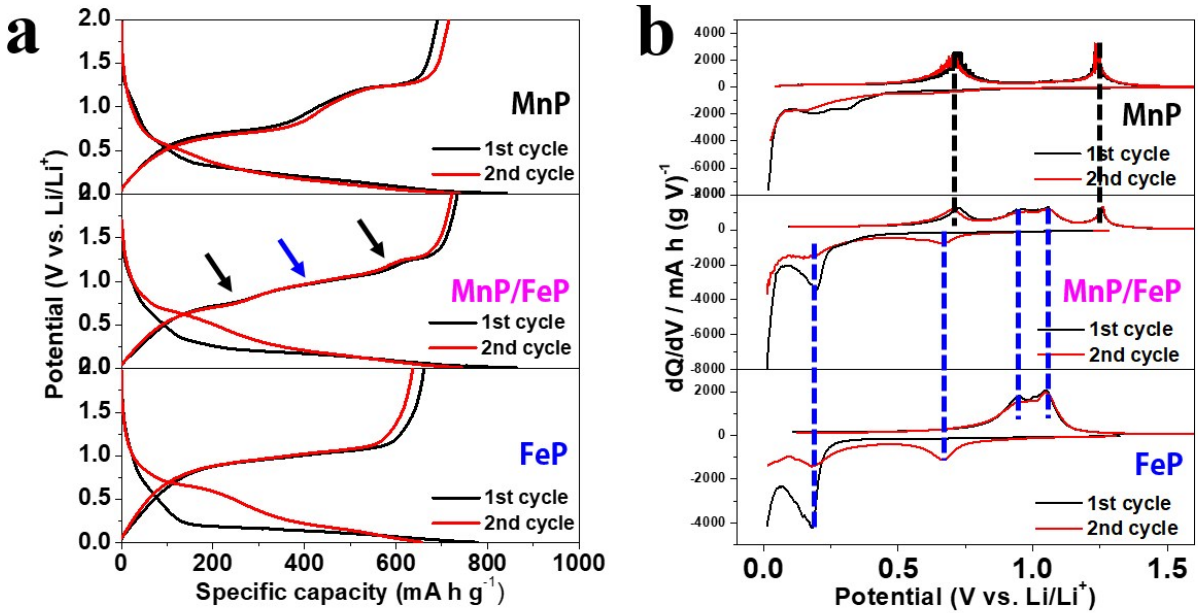

Fig. S4 (a) Galvanostatic discharge/charge profiles and (b) corresponding differential capacity plots (DCPs) of MnP, MnP/FeP mixture, and FeP electrodes.

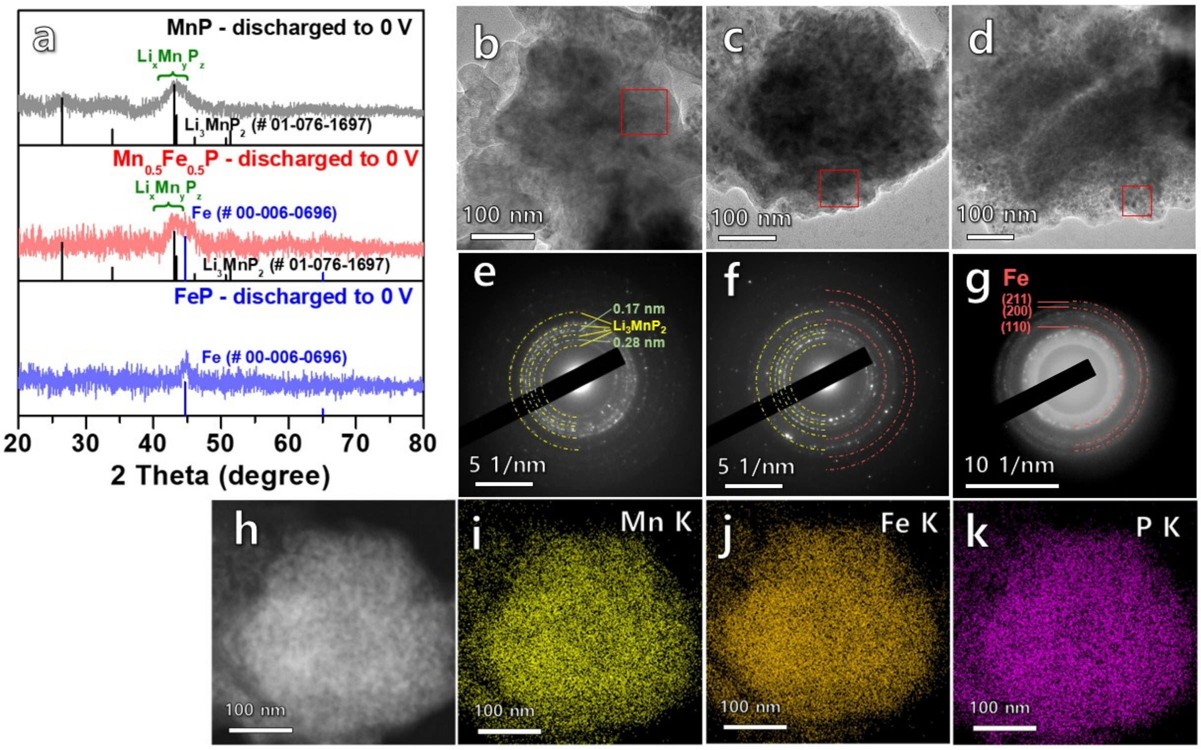

Fig. S5 (a) *Ex-situ* XRD patterns, TEM images, and SAED patterns of fully discharged states of (b,e) MnP, (c,f) $Mn_{0.5}Fe_{0.5}P$, and (d,g) FeP electrodes, and (h) STEM image and (i-k) EDS mapping (Mn K, Fe K, and P K) of (c) $Mn_{0.5}Fe_{0.5}P$ electrode.

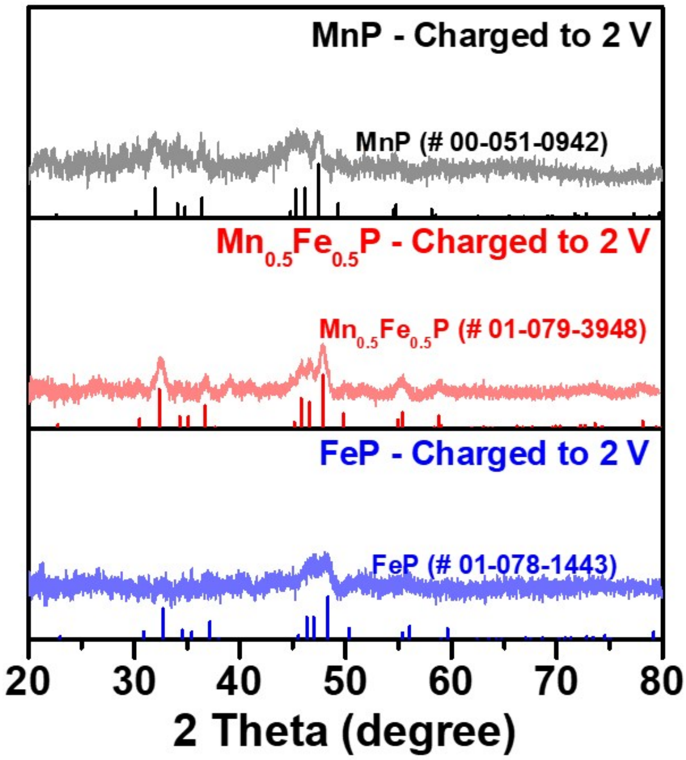

Fig. S6 *Ex-situ* XRD patterns of 1st fully charged states for $Mn_{1-x}Fe_xP$ (x = 0, 0.5, and 1.0) electrodes. The reference peaks for MnP (ICDD # 00-051-0942, black color), $Mn_{0.5}Fe_{0.5}P$ (ICDD # 01-079-3948, red color), and FeP (ICDD # 01-078-1443, blue color) are included.

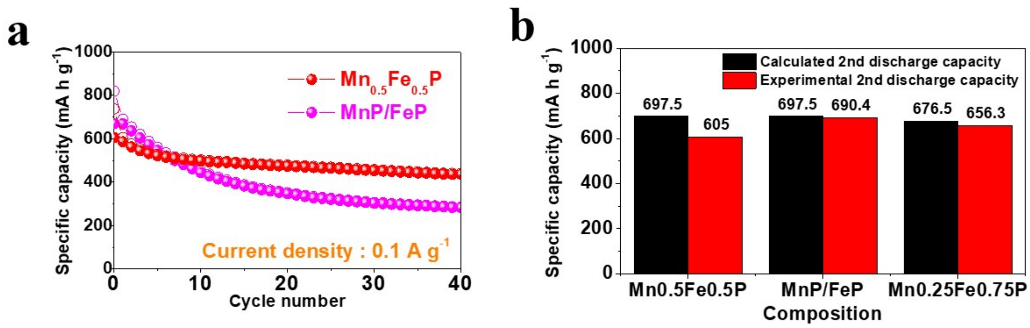

Fig. S7 (a) Cycle performance of $Mn_{0.5}Fe_{0.5}P$ solid solution and MnP/FeP mixture electrodes at the current density of 100 mA g^{-1} and (b) comparison of experimentally determined and expected 2nd discharge capacity in $Mn_{0.5}Fe_{0.5}P$ and $Mn_{0.25}Fe_{0.75}P$ solid solution and MnP/FeP mixture electrodes. The expected values were estimated from the reversible capacities of both MnP and FeP electrodes.

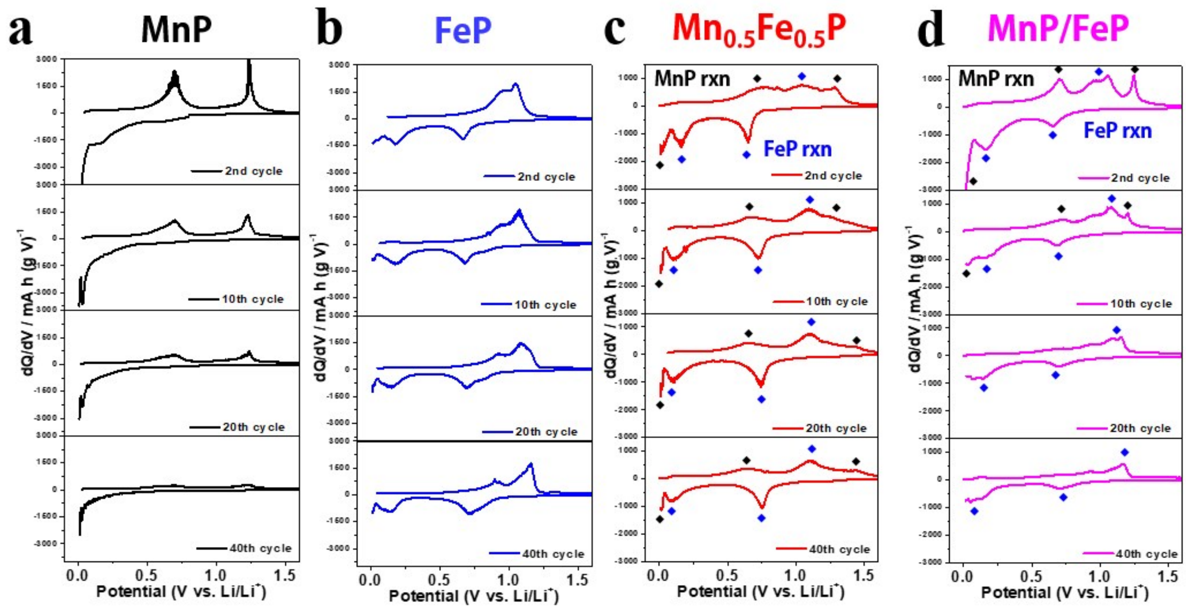

Fig. S8 DCPs for MnP, FeP, $Mn_{0.5}Fe_{0.5}P$, and MnP/FeP electrodes for 2nd, 10th, 20th, and 40th cycles at the current density of 100 mA g^{-1}.

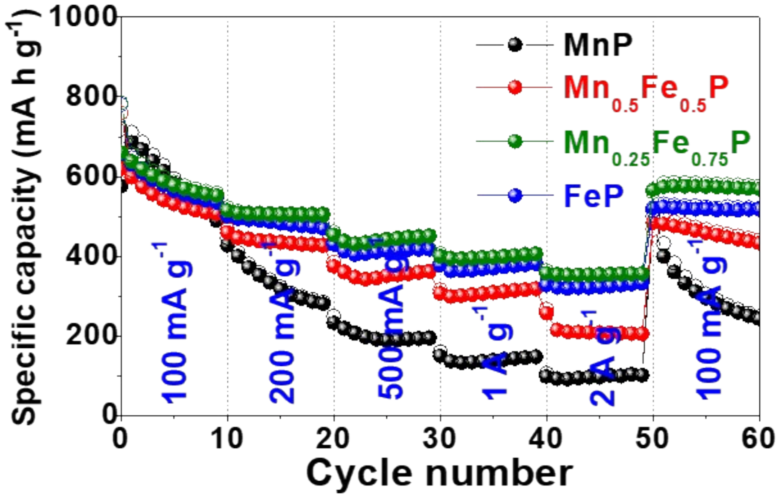

Fig. S9 (a) Rate capabilities of the $Mn_{1-x}Fe_xP$ (x = 0, 0.5, 0.75, and 1) electrodes.

Fig. S10 Lithium storage performance comparison of $Mn_{0.25}Fe_{0.75}P$ solid solution electrode with the previously reported FeP and MnP-based electrodes.

Materials	Current density (mA g^{-1})	Capacity (mA h g^{-1})	Cycle number (cycle retention)	Ref.
MnP nanorod	144 1440 3600	350 200 150		[1]
MnP powder	50	287	50 (33%)	[2]
MnP nanoparticle	120	289	10 (80%)	[3]
FeP spheroidal particle	100 1000	600 300		[4]
FeP nanoplate	200	350	100 (60%)	[5]
FeP nanosphere	200	207	100 (23%)	[6]
$Mn_{0.25}Fe_{0.75}P$ nanoparticle	100 1000 2000	506 464 370	40 (76%) 60 (97%) 100 (99%)	This work

[1] P. Mei, J. Lee, M. Pramanik, A. Alshehri, J. Kim, J. Henzie, J. Kim, Y. Yamauchi, *ACS Appl. Mater. Inter.* 2018, **10**, 19739-19745.

[2] L. Li, Y. Peng, H. Yang, *Electrochimica Acta.* 2013, **95**, 230-236.

[3] S. Sim, J. Cho, *J. Electrochem. Soc.* 2012, **159(5)**, A669-A672.

[4] P. S. Veluri, S. Mitra, *RSC advance*, 2016, **6**, 87675-87679.

[5] F. Han, C. Zhang, J. Yang, G. Ma, K. He, X. Li, *J. Mater. Chem. A.* 2016, **4**, 12781-12789.

[6] X. Wang, K. Chen, G. Wang, X. Liu, H. Wang, *ACS Nano.* 2017, **11**, 11602-11616.

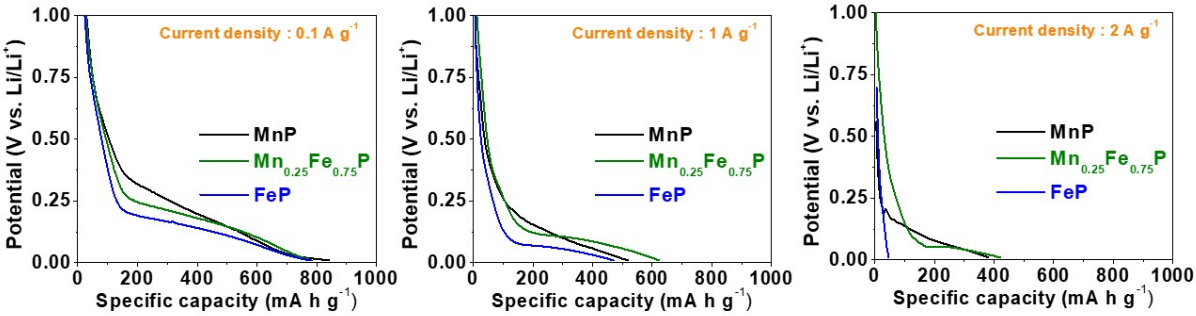

Fig. S11 Galvanostatic discharge voltage profiles of $Mn_{1-x}Fe_xP$ (x = 0, 0.75, and 1) electrodes for 1st cycle at 0.1, 1.0, and 2.0 A g^{-1}, respectively.

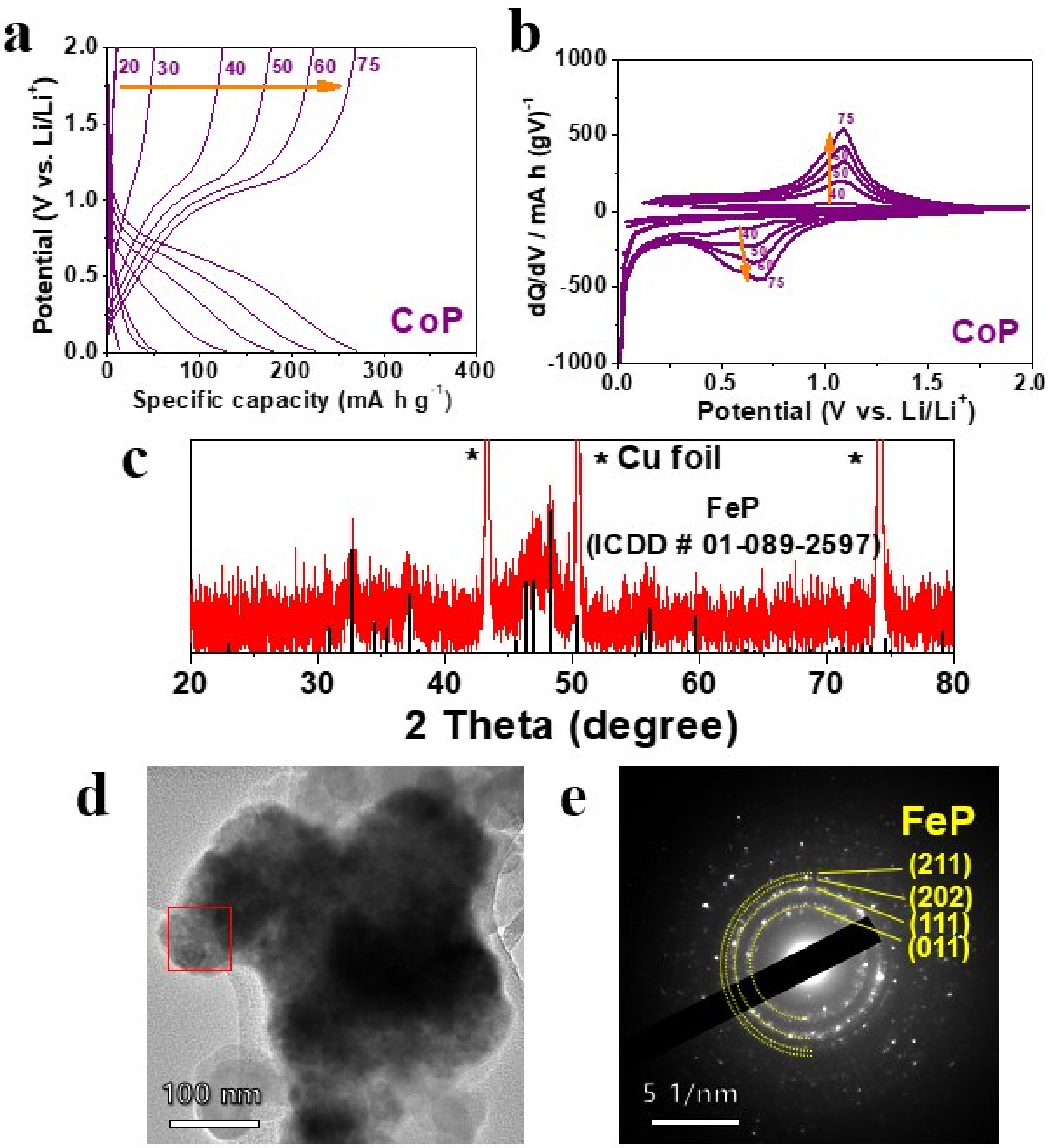

Fig. S12 (a) Galvanostatic voltage profiles and (b) corresponding differential capacity plots (DCPs) of CoP electrode at 2 A g^{-1} and (c) XRD pattern, (d) TEM image, and (e) SAED pattern of FeP electrode for 1st fully discharged state at 2 A g^{-1}.

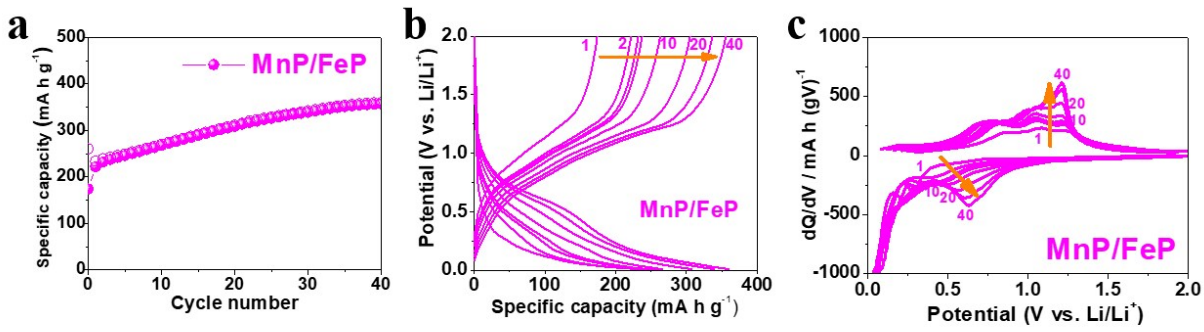

Fig. S13 (a) Cycling performance of MnP/FeP electrode at 2 A g^{-1} and corresponding (b) galvanostatic voltage profiles and (c) differential capacity plots (DCP).

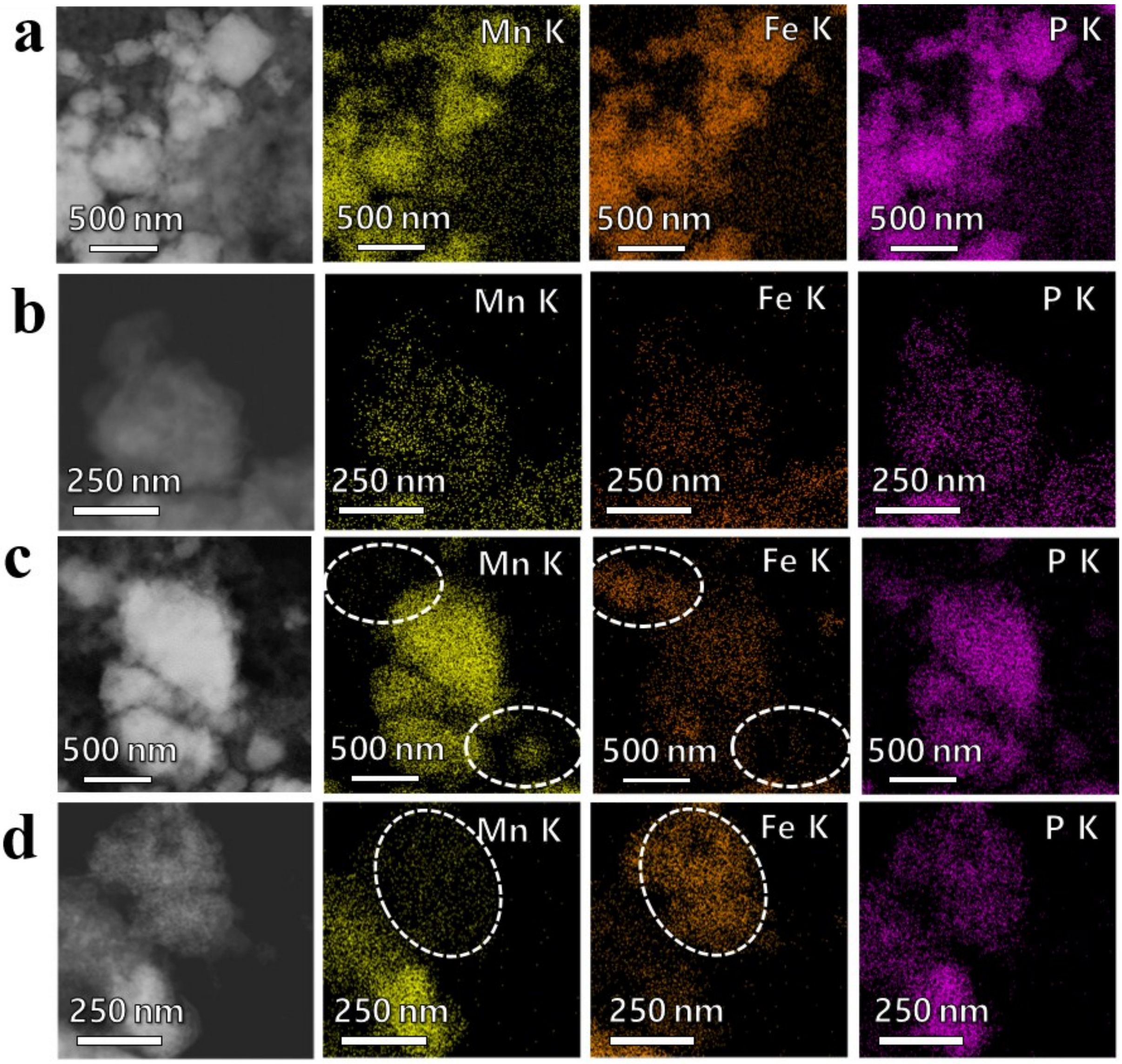

Fig. S14 STEM images and EDS mapping images (Mn K, Fe K, and P K) of after 1st and 100th cycled electrodes tested at 2 A g^{-1} for (a,b) $Mn_{0.5}Fe_{0.5}P$ and (c,d) MnP/FeP electrodes.