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

Supplementary information: A sol-gel route to titanium nitride conductive coatings on battery materials and performance of TiN-coated $LiFePO_4$

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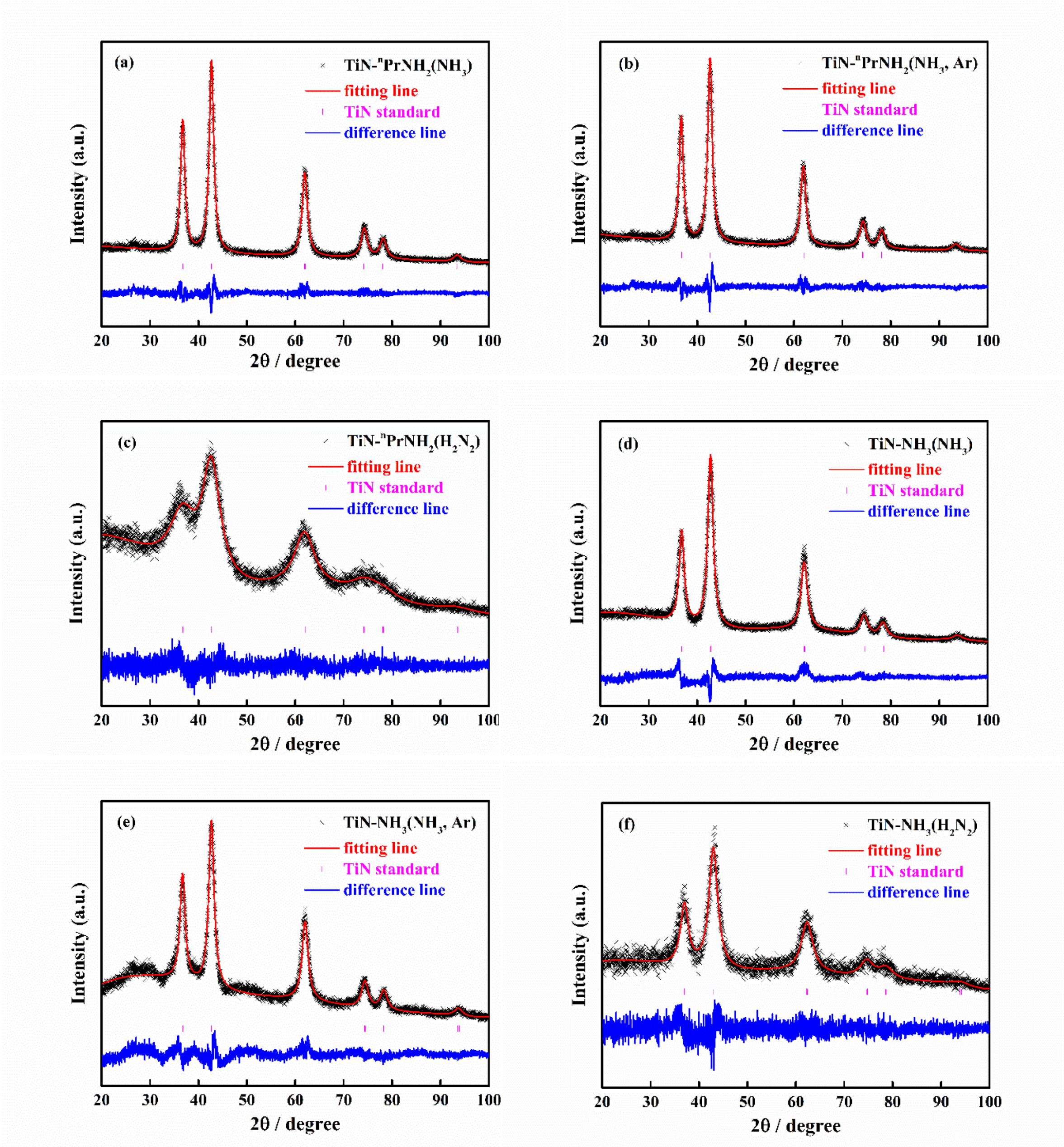

Fig. S1 Rietveld fits to the XRD patterns of (a) TiN-^{n}PrNH$_2$(NH$_3$) (R_{WP} = 9.44% and R_p = 7.29%), (b) TiN-^{n}PrNH$_2$(NH$_3$, Ar) (R_{WP} = 9.92% and R_p = 7.77%), (c) TiN-^{n}PrNH$_2$(H$_2$N$_2$) (R_{WP} = 8.44% and R_p = 6.37%), (d) TiN-NH$_3$(NH$_3$) (R_{WP} = 9.65% and R_p = 7.71%), (e) TiN-NH$_3$(NH$_3$, Ar) (R_{WP} = 9.93% and R_p = 7.90%) and (f) TiN-NH$_3$(H$_2$N$_2$) (R_{WP} = 18.88% and R_p = 14.47%) samples. The data points and Rietveld fits are overlaid in black crosses and red lines, respectively. The difference plots are shown in blue. The pink tick marks represent the allowed reflection positions for TiN with space group $Fm\bar{3}m$.

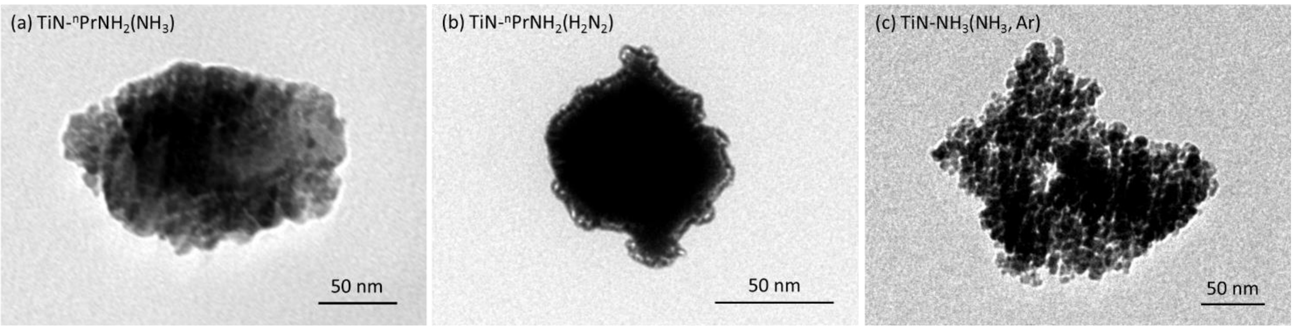

Fig. S2 TEM images (scale bar = 50 nm) of (a) TiN-^{n}PrNH$_2$(NH$_3$), (b) TiN-^{n}PrNH$_2$(H$_2$N$_2$) and (c) TiN-NH$_3$(NH$_3$, Ar) samples.

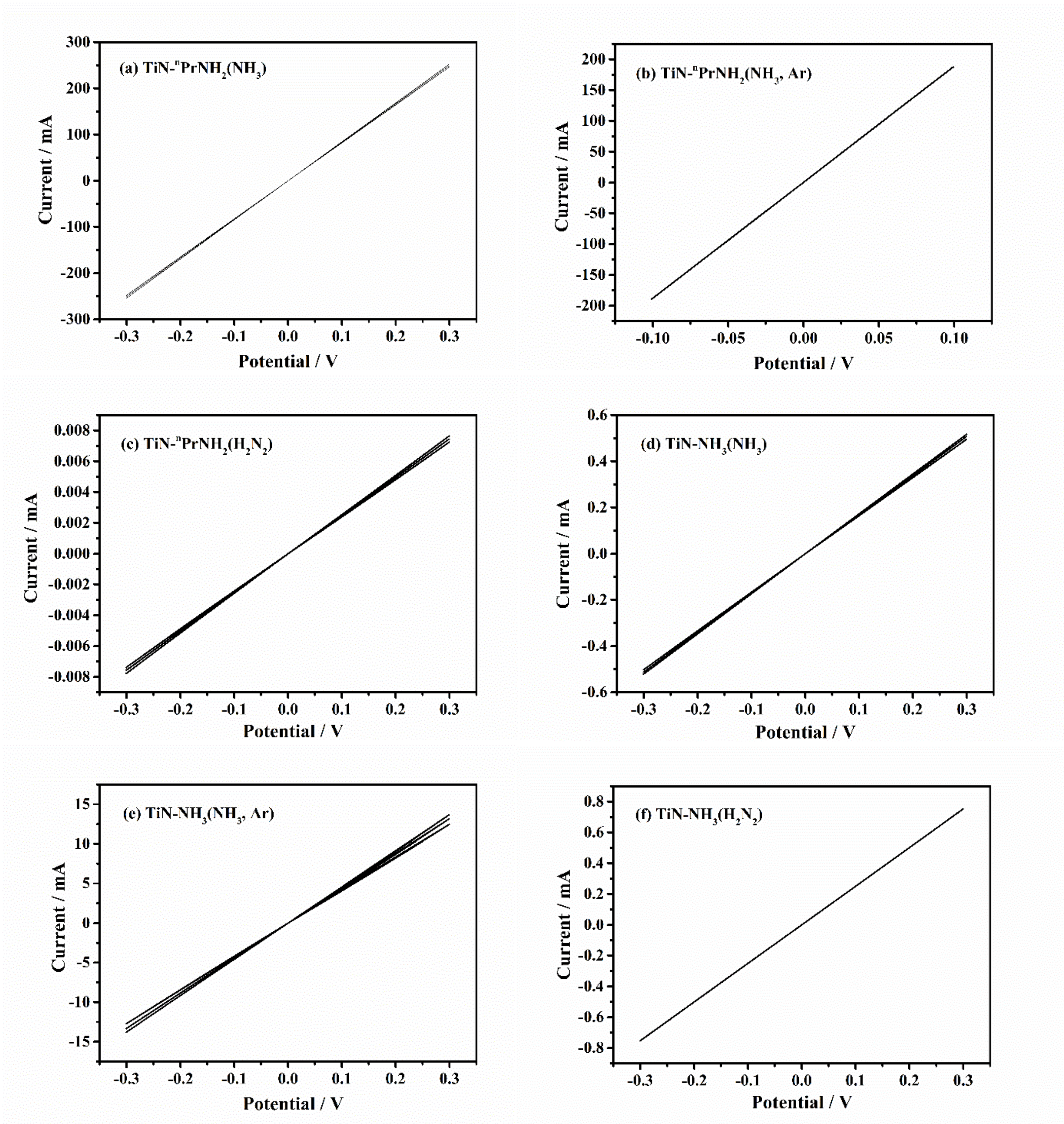

Fig. S3 Current-potential plots for dry (a) TiN-^{n}PrNH$_2$(NH$_3$), (b) TiN-^{n}PrNH$_2$(NH$_3$, Ar), (c) TiN-^{n}PrNH$_2$(H$_2$N$_2$), (d) TiN-NH$_3$(NH$_3$), (e) TiN-NH$_3$(NH$_3$, Ar) and (f) TiN-NH$_3$(H$_2$N$_2$) samples at scanning rate of 20 mV s^{-1}.

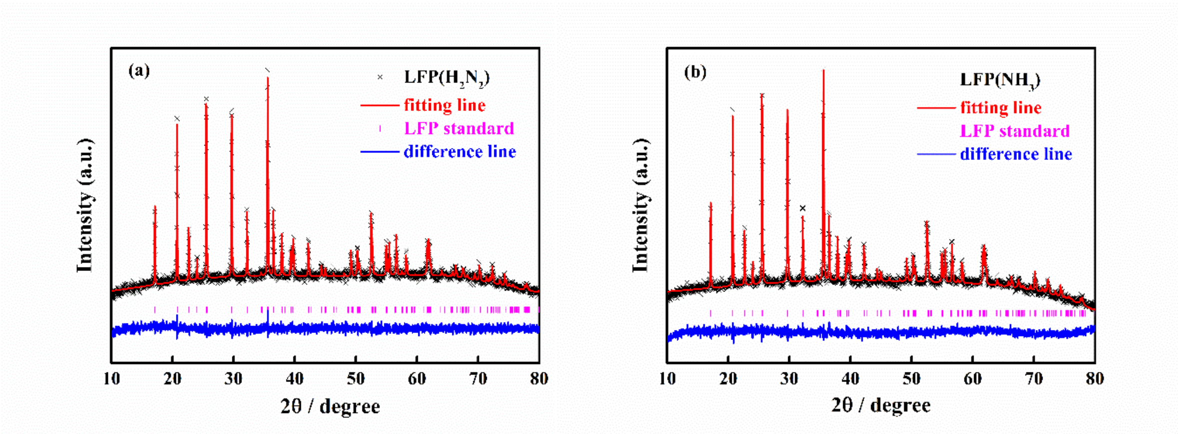

Fig. S4 Rietveld fits to the XRD patterns of (a) LFP(H_2N_2) (R_{WP} = 2.29% and R_p = 1.82%) and (b) LFP(NH_3) (R_{WP} = 1.96% and R_p = 1.55%) samples. The data points and Rietveld fits are overlaid in black crosses and red lines, respectively. The difference plots are shown in blue. The pink tick marks represent the allowed reflection positions for $LiFePO_4$ with space group *Pnma*.

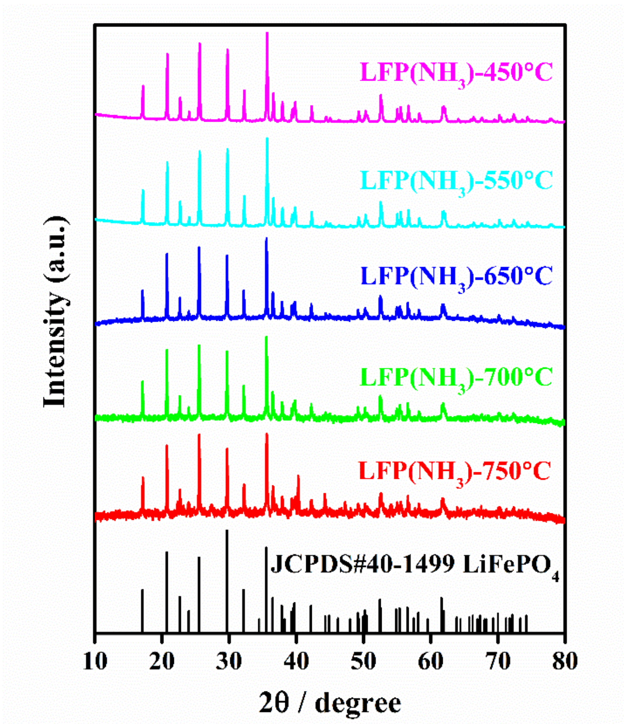

Fig. S5 XRD patterns of LFP(NH_3)-450°C, LFP(NH_3)-550°C, LFP(NH_3)-650°C, LFP(NH_3)-700°C and LFP(NH_3)-750°C samples prepared by hydrothermal method and heated under NH_3 at the temperature of 450 °C to 750 °C. The black stick pattern denotes the literature positions and intensities of $LiFePO_4$ reflections.

Table S1 Lattice parameters obtained from the Rietveld fits of XRD patterns for LFP(NH_3)-450°C, LFP(NH_3)-550°C, LFP(NH_3)-650°C, LFP(NH_3)-700°C, LFP(NH_3)-750°C and LFP(H_2N_2)samples.

Sample	a (Å)	b (Å)	c (Å)
LFP(NH_3)-450°C	10.3232(2)	6.0015(1)	4.6890(8)
LFP(NH_3)-550°C	10.3216(1)	6.0022(9)	4.6904(8)
LFP(NH_3)-650°C	10.3254(2)	6.0057(1)	4.6938(1)
LFP(NH_3)-700°C	10.3233(3)	6.0061(2)	4.6930(2)
LFP(NH_3)-750°C	10.3246(6)	6.0082(3)	4.6958(3)
LFP(H_2N_2)	10.3274(2)	6.0060(1)	4.6919(1)

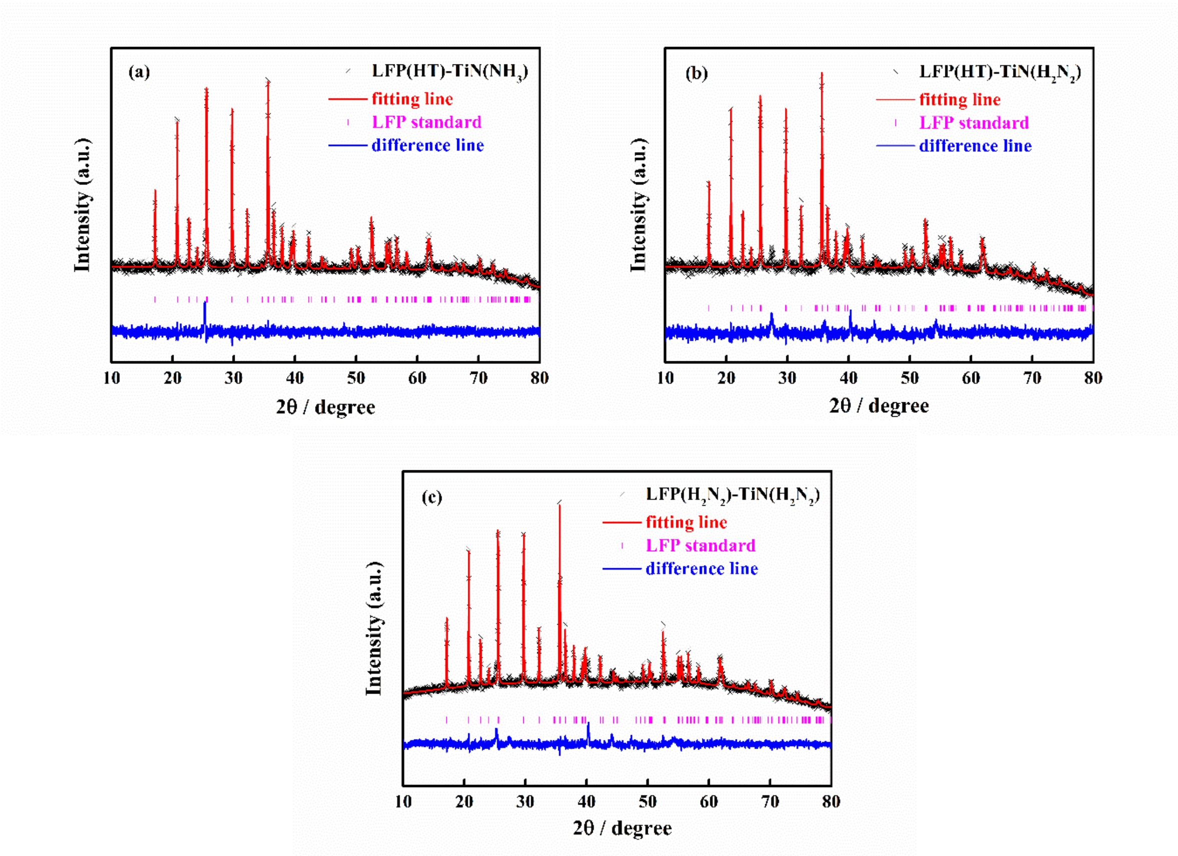

Fig. S6 Rietveld fits to the XRD patterns of (a) LFP(HT)-TiN(NH_3) (R_{WP} = 2.45% and R_p = 1.86%), (b) LFP(HT)-TiN(H_2N_2) (R_{WP} = 2.69% and R_p = 2.03%) and (c) LFP(H_2N_2)-TiN(H_2N_2) (R_{WP} = 2.36% and R_p = 1.73%) samples. The data points and Rietveld fits are overlaid in black crosses and red lines, respectively. The difference plots are shown in blue. The pink tick marks represent the allowed reflection positions for $LiFePO_4$ with space group *Pnma.*

Table S2 Lattice parameters and crystallite sizes of $LiFePO_4$ obtained from the Rietveld fits of XRD patterns for LFP(HT)-TiN(NH_3), LFP(HT)-TiN(H_2N_2), LFP(H_2N_2)-TiN(NH_3) and LFP(H_2N_2)-TiN(H_2N_2) samples.

Sample	$LiFePO_4$			
	a (Å)	b (Å)	c (Å)	Crystallite size (nm)
LFP(HT)-TiN(NH_3)	10.3267(3)	6.0052(2)	4.6939(2)	123(2)
LFP(HT)-TiN(H_2N_2)	10.3195(4)	6.0009(2)	4.6951(2)	173(5)
LFP(H_2N_2)-TiN(NH_3)	10.3249(1)	6.00473(4)	4.69113(3)	153(1)
LFP(H_2N_2)-TiN(H_2N_2)	10.3168(3)	6.0021(1)	4.6938(1)	175(3)

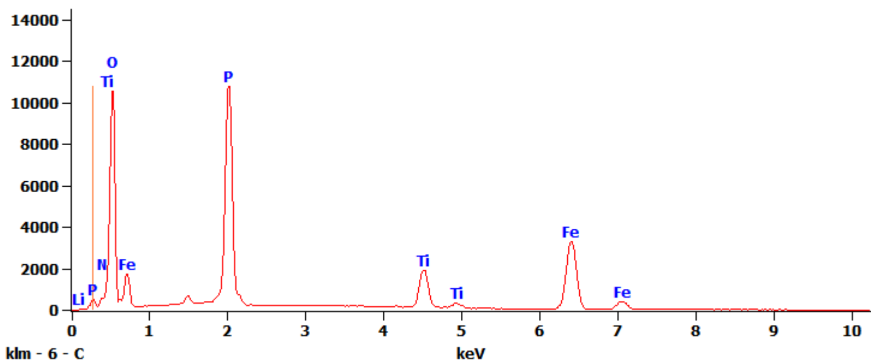

Fig. S7 EDS spectrum of LFP(H_2N_2)-TiN(NH_3) sample.

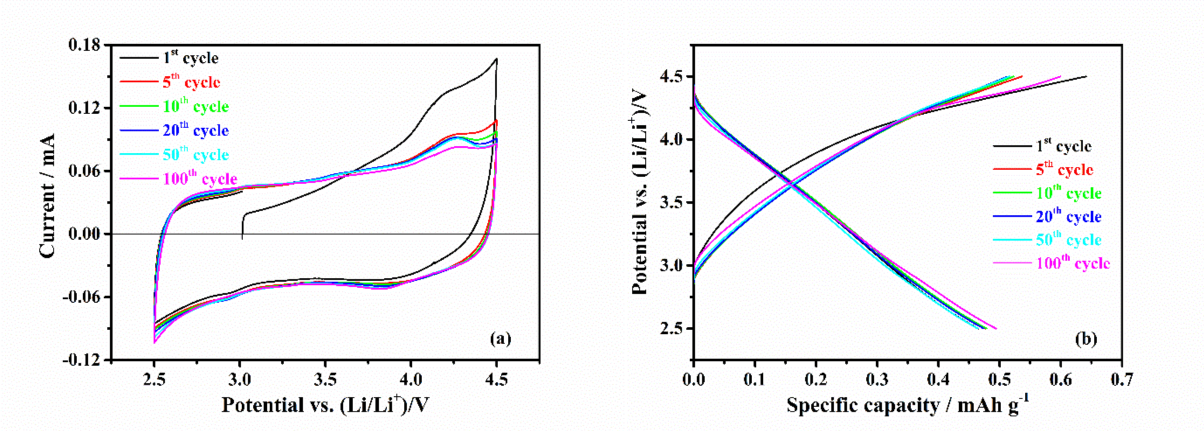

Fig. S8 (a) Cyclic voltammetry plots of TiN-^{n}PrNH$_2$(NH$_3$)/Li half cell at 20 mV s^{-1} over the range of 1 to 5 V at room temperature; (b) The voltage profile against specific capacity of TiN-^{n}PrNH$_2$(NH$_3$)/Li half cell under galvanostatic cycling between 2.5 and 4.5 V for 100 cycles.