Electronic Supplementary Information (ESI)

Poly(ethyleneimine) modified TiO_2 nanorods for adsorptive recovery of Lithium from battery cathode and brine solution

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1. UV-Vis Spectrophotometric analysis of Lithium using Thorin

Lithium estimation was done using Thorin (Disodium 4-[2-(2-arsonophenyl)

hydrazin-1-ylidene]-3-oxo-3,4 dihydronaphthalene-2,7-disulfonate) as a complexing agent in the presence of a highly basic medium, it forms a stable orange-coloured complex;[1] for this analysis, 0.2 % Thorin was prepared by dissolving 0.2 g of Thorin in 100 mL of Deionised water. 20 % w/w KOH was prepared by dissolving 4g of KOH in 20 mL. Before the analysis, Lithium sample solutions ranging from 2 ppm to 10 ppm were prepared with proper dilutions. Initially, 0.1 mL of KOH, followed by 0.2 mL of Lithium sample solution, 0.1 mL of Thorin, and 7 mL of acetone, were added in a 10 mL standard flask and made up to the mark with water to achieve a total volume of 10 mL. A reagent blank (10 mL) was also prepared without the addition of the analyte. The mixture was kept undisturbed for about 35min

after which the UV measurements were taken. Upon addition of lithium, it undergoes complexation with the Thorin, causing a Bathochromic shift as observed in the spectrum (Fig.S1). The λ_{max} of the Thorin reagent blank was found to be 443 nm, and that of the Lithium Thorin complex was at 473 nm. A linear calibration graph was developed for the same, as shown in (Fig.S1), and the regression coefficient (R^2) was found to be 0.966.

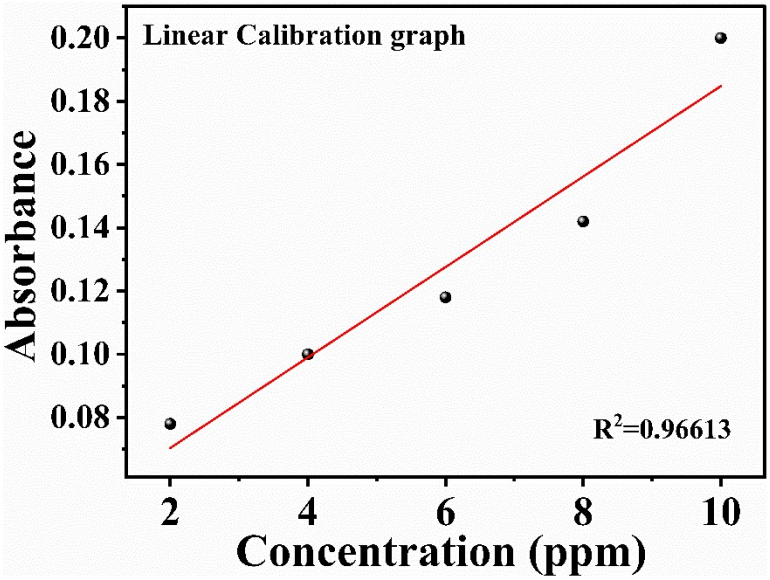

Fig S1. Linear calibration plot using UV-spectrophotometry

2. Analysis of lithium using Ion-Chromatography

Lithium was also quantified with the help of Ion Chromatography. Metrohm 883 Basic IC Plus paired with a conductivity detector was used, and the column utilized for estimation was Nucleosil 5SA-125/4.0, where the stationary phase is a polymer functionalized with negatively charged sulphonate groups (-SO_3) that help with the cation exchange. The eluent that was used was 7.5mmol/L Nitric acid and 4.0 mmol/L Tartaric Acid, prepared by dissolving 475 µL of HPLC grade conc. Nitric acid, 0.600 g of Tartaric acid and dissolving it in 1000 mL of Milli-Q water, which was then filtered through a PVDF filter of pore size 0.45µ into a standard eluent

bottle after which it was degassed in an ultrasonicator bath for 10 min and then used. Lithium sample solutions of known concentrations ranging from 2 ppm to 10 ppm were used to build the calibration graph, as shown in (Fig.S2). Retention time was found to be 8.3 µS/cm. A linear calibration graph was developed for the same, where the regression coefficient (R^2) was found to be 0.9866.

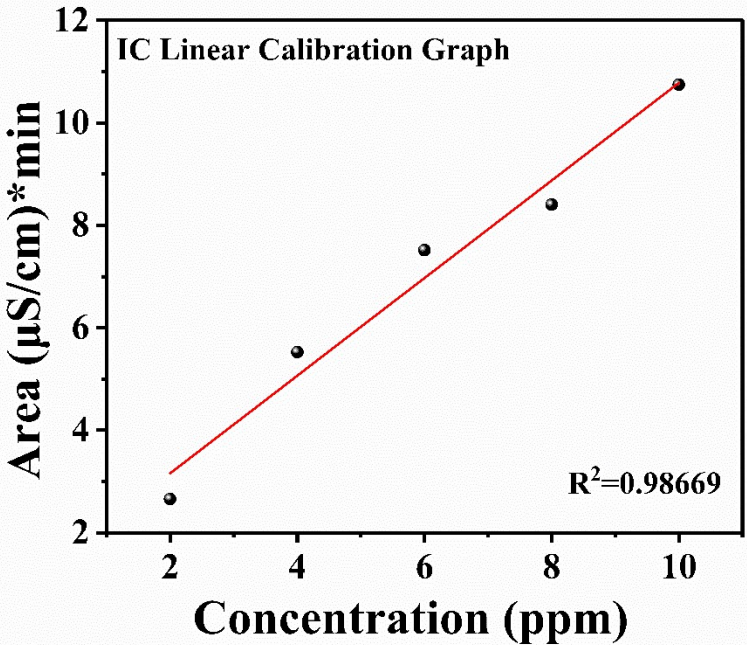

Fig S2. Linear calibration plot obtained using Ion-Chromatography

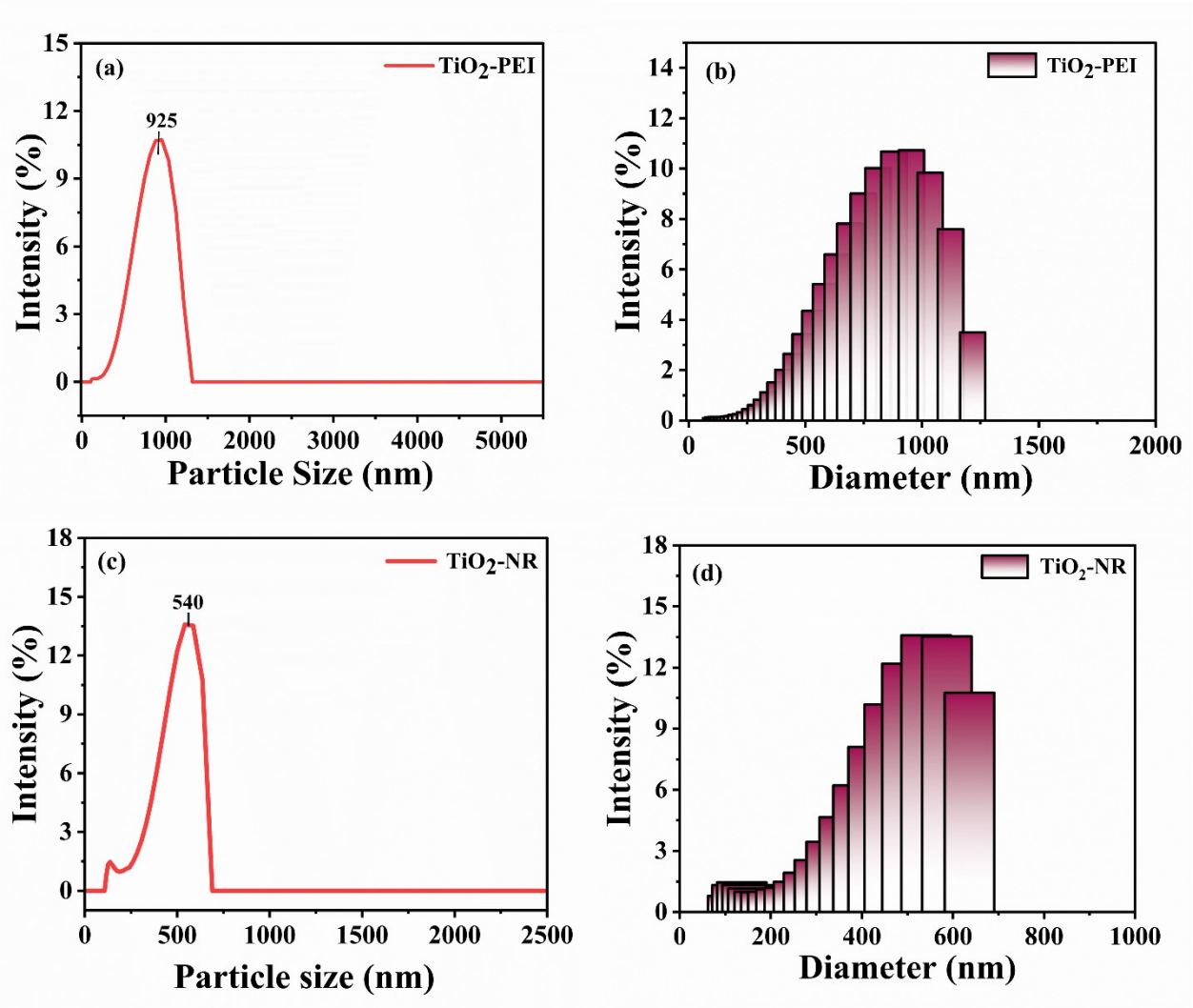

Fig S3. (a) DLS particle size distribution curve of TiO_2-NR (b) DLS particle size distribution histogram of TiO_2-NR (c) DLS particle size distribution curve of TiO_2(NR)-PEI (d) DLS particle size distribution histogram of TiO_2(NR)-PEI

3. Comparison of the adsorption capacity with TiO_2(NR) and TiO_2(NR)-PEI

Adsorption was carried out by taking 10 ppm of lithium solution in a centrifuge tube with 0.15 g of adsorbent and kept for adsorption using a conventional stirring method on a vortex shaker for 180 min at 720 rpm. It has been observed that when TiO_2(NR) was used, there was 39% adsorption, and when TiO_2(NR)-PEI was used, 91% adsorption was observed. Thus, a synergistic contribution of the TiO_2(NR) and PEI led to lithium adsorption. It is

evident from the absorption spectra (Fig S4) that the inclusion of PEI brings about a significant dynamic change, resulting in the effective adsorption of Li on the PEI-anchored TiO_2 surface.

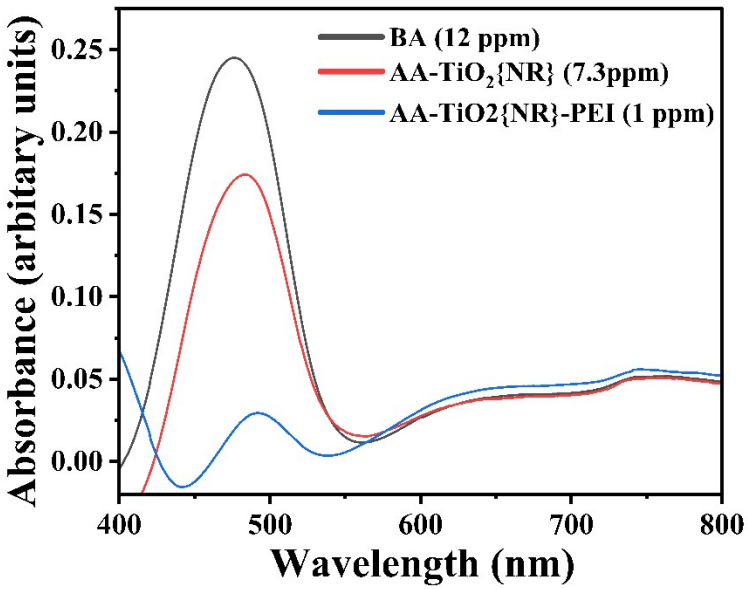

Fig S4: UV-Vis Spectrum for the adsorption of lithium using (a) TiO_2{NR} and (b) TiO_2{NR}-PEI where BA refers to Before adsorption and AA refers to After adsorption.

Table S1. Isotherm parameters for Lithium adsorption

Isotherm models	Isotherm parameters	Values
Langmuir	q_{max} (mg g^{-1})	2.703
	K_L (L mg^{-1})	0.0535
	R^2	0.998
Freundlich	K_F ($mg^{1-1/n}$ g^{-1} $L^{1/n}$)	0.955
	n	4.545
	R^2	0.996
Temkin	b_T (J mol^{-1})	75.07 $\times 10^{-2}$
	K_T (L g^{-1})	2.13 $\times 10^{3}$
	R^2	0.933

Table S2. Kinetic parameters for the adsorption of Lithium.

Kinetics models	Parameters	Values
pseudo–first order	k_1 (min^{-1})	0.0033
	q_{e1} (mg g^{-1})	2.667
	R^2	0.981
pseudo-second order	k_2 (g mg^{-1} min^{-1})	0.011
	q_{e2} (mg g^{-1})	2.326
	R^2	0.944
Intra–particle diffusion	C_1 (mg g^{-1})	0.329
	K_{i1} (mg g^{-1} $min^{1/2}$)	0.095
	R^2	0.998

	C_2 (mg g^{-1}) K_{i2} (mg g^{-1} min$^{1/2}$) R^2	0.291 0.113 0.997

Table S3. Thermodynamic parameters (enthalpy, entropy, and free energy changes) for the adsorption of Lithium.

Temperature (Kelvin)	ΔG^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (kJ mol^{-1} K^{-1})	R^2
303	-1.106	15.589	0.0549	0.9613
313	-1.899			
323	-2.401			
333	-2.667			

Table S4. Comparison table of Lithium Adsorption performance with other adsorbents.

Sl.No	Adsorbent used	pH, Time required	Adsorption Capacity (mg g^{-1})	Reference
1.	AN[a]: Amberlite sodium form	7, 24 h	4.1	[2]
2.	Li/AL – LDH (D)	Acidic and Basic, 3.3 h	4.0	[3]
3.	Lithium aluminium hydroxide	10 h	5.90	[4]
4.	Fe_3O_4 nanoparticles coated LDH-MLDH 4	4, 5 h	4.06	[5]
5.	LiCl · 2Al (OH)$_3$ · nH2O	4 h	3.0	[6]
6.	**TiO_2(NR)-PEI**	11, 3 h	2.76	**(This study)**

Table S5. Elemental composition from the EDS spectra.

Element	Line Type	Apparent Concentr-ation	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard
O	K series	76.54	0.25757	46.00	0.15	71.83	SiO_2	Yes
Ti	K series	242.21	2.42214	54.00	0.15	28.17	Ti	Yes
Total:				100.00		100.00		

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