Supplementary Material

Insights into the Stability and Reactivity of Lithiated Si-binder Interfaces for Next Generation Lithium-Ion Batteries

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April 15, 2024

System	atom	without Li	8 Li	16 Li	24 Li
Si-110	Si1	3.83	3.94	3.96	4.19
	Si2	3.81	3.95	3.96	4.19
Si-111	atom	without Li	10 Li	20 Li	30 Li
	Si1	3.83	3.85	3.98	4.09
	Si2	4.11	4.13	4.11	4.11

Table 1S: Löwdin charges of Si atoms for Si-110 and Si-111 systems with different numbers of Li content, compared with Si-slab without Li.

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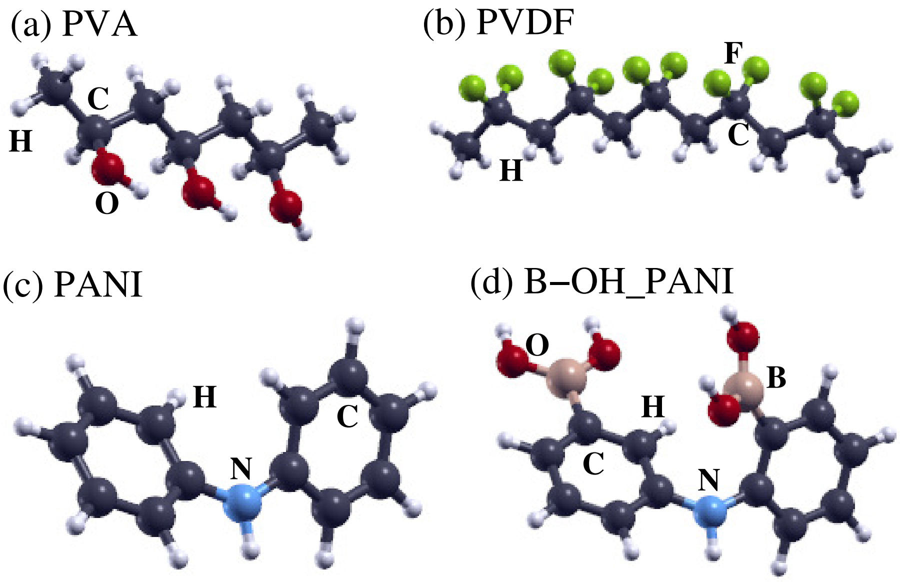


Figure 1S: Molecular structure of the monomers used in this study: (a) polyvinyl alcohol (PVA) (b) polyvinylidene fluoride (β-PVDF), (c) polyaniline (PANI), and (d) boronic acid functional group in polyaniline (B-OH_PANI).

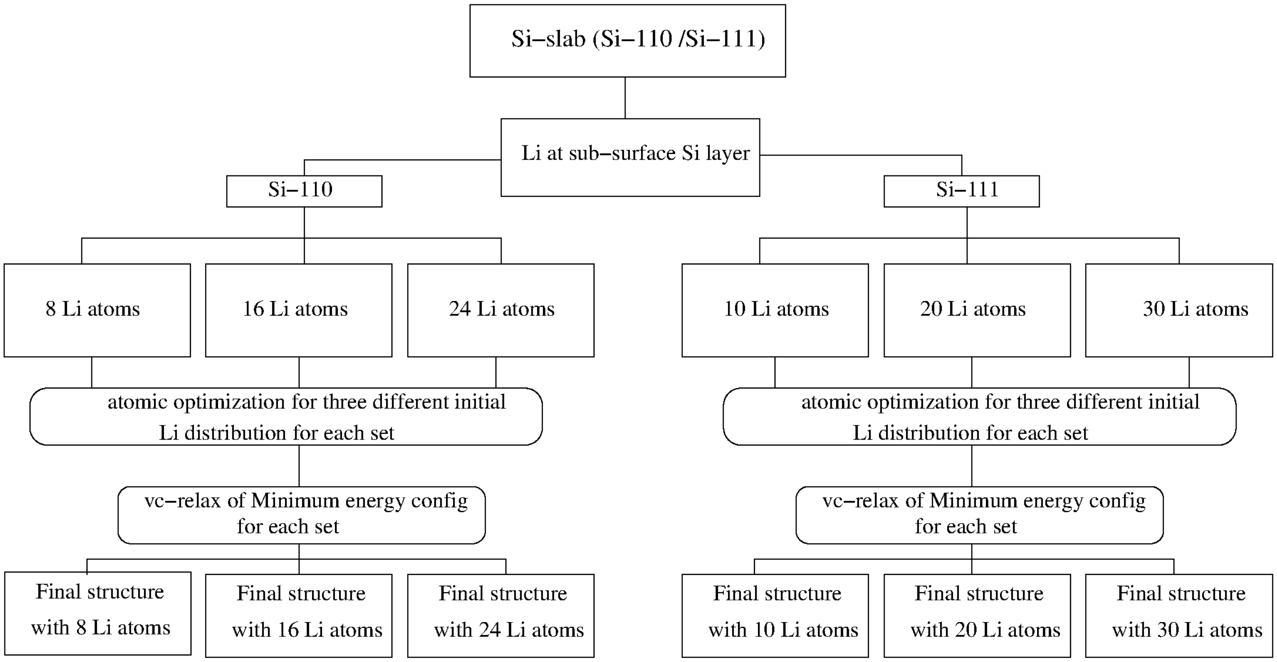


Figure 2S: Calculation details that followed to generate all optimized lithiated Si-surfaces

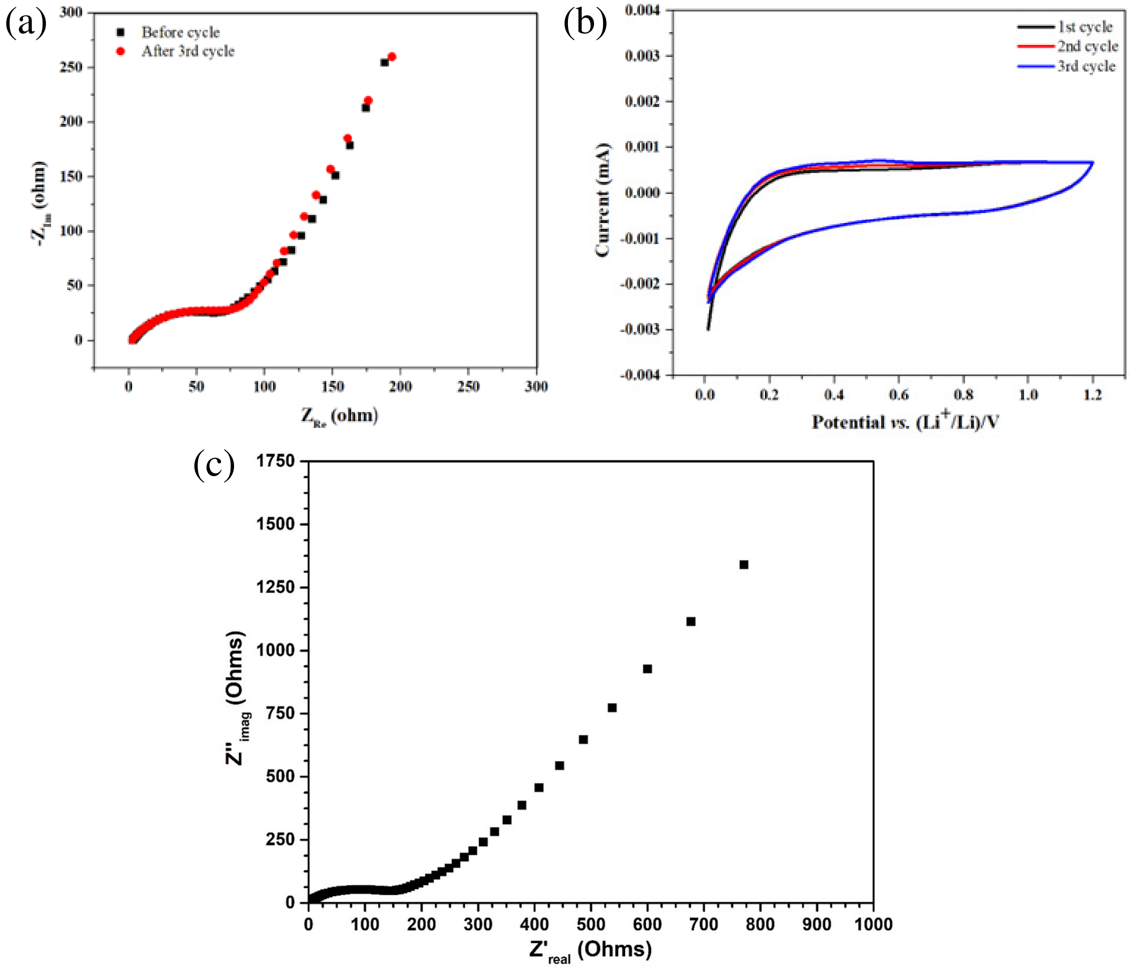


Figure 3S: (a) Electrochemical Impedance Spectroscopy (EIS) of B-OH_PANI-PVA, (b) CV of B-OH_PANI-PVA, (c) Electrochemical Impedance Spectroscopy (EIS) of PVDF

When the EIS spectra of B-OH PANI+PVA and PVDF are compared, it is seen that B-OH PANI+PVA shows lower impedance meaning it is more conductive (Figure 3S (a) and 3S(c)). As a result (3S (b)) of cyclic voltammetry, it is understood that B-OH PANI+PVA is electrochemically stable since it does not have any anodic or cathodic peaks.

System	Binder	atom	without Li	with Li	Li + binder
16 Li-Si-110	PVA + B-OH_PANI	Si1	3.83	3.96	3.54
		Si2	3.81	3.96	3.80
	PVA + β-PVDF	Si1	3.81	3.96	4.25
		Si2	3.85	4.13	3.62
	PVA + PANI	Si1	3.83	4.19	3.94
		Si2	3.83	3.96	3.50
20 Li-Si-111	PVA + B-OH_PANI	Si1	3.83	3.98	3.72
		Si2	4.11	4.11	4.19
	PVA + β-PVDF	Si1	3.86	4.01	3.43
		Si2	4.12	4.11	3.86
	PVA + PANI	Si1	3.87	4.09	4.14
		Si2	4.12	4.11	4.08

Table 2S: Löwdin charges of Si atoms for 16 Li-Si-110 and 20 Li-Si-111 systems with co-binders, compared with bare lithiated Li-Si surface and Si-slab only.

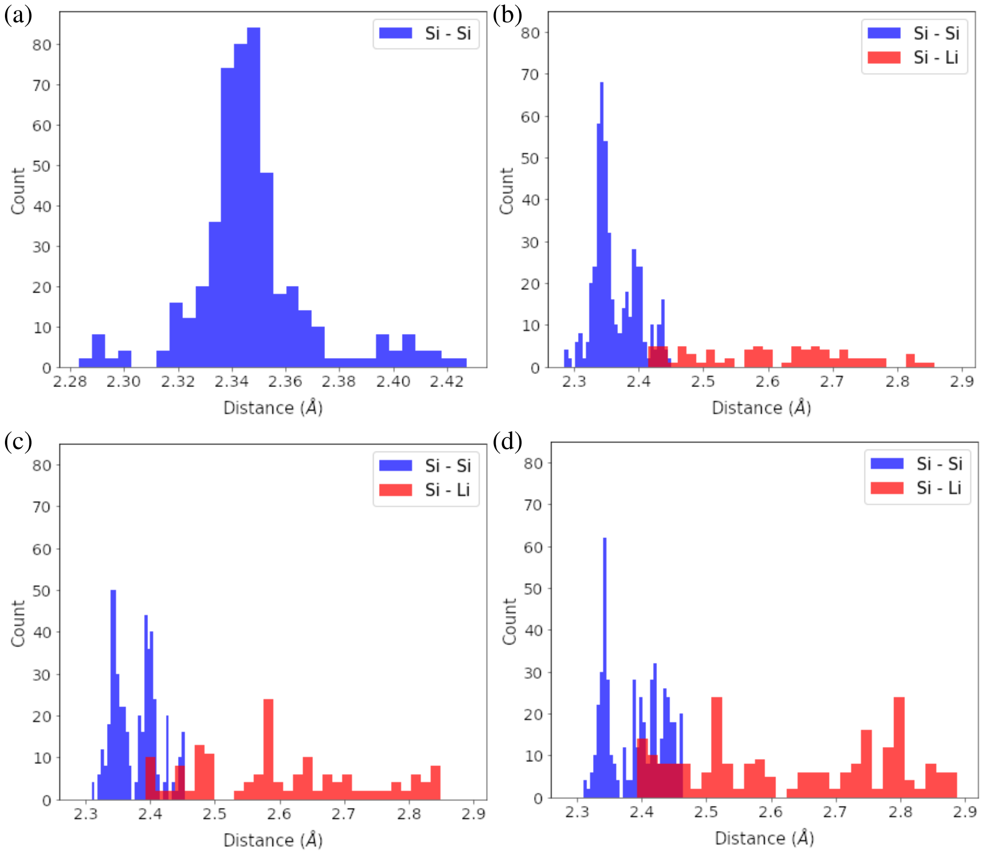


Figure 4S: Distribution of Si-Si and Si-Li nearest neighbour distances (Å) considering above four layers of (a) Si-110, (b) 8 Li-Si-110, (c) 16 Li-Si-110 and (d) 24 Li-Si-110.

System	Density(kg/m^3)		
	Simulation	Experimental	CAS density (e)
PANI	978 - 1289 (a)	1245 (b)	1245
PVA	1290 (c)	1293 (c)	1190 - 1310
β-PVDF	1590 (d)	1660 - 1780 (d)	370

Table 3S: Reference for density of polymer used here: PVA, PANI, β-PVDF.

References:

(a) Manel Canales, David Curcó, and Carlos Alemán J. Phys. Chem. B, 114, 30, 9771–9777 (2010).

(b) Jaroslav Stejskal, and Irina Sapurina, Pure and Applied Chemistry, 77, 5, 815-826 (2005).

(c) J. S. Bermejo, C. M. Ugarte, Macromol. Theory Simul., 18, 317-327 (2009).

(d) Jie Yang, Xiaohu Yao, Zhaoxu Meng, Polymer 245, 124691 (2022).

(e) https://commonchemistry.cas.org/

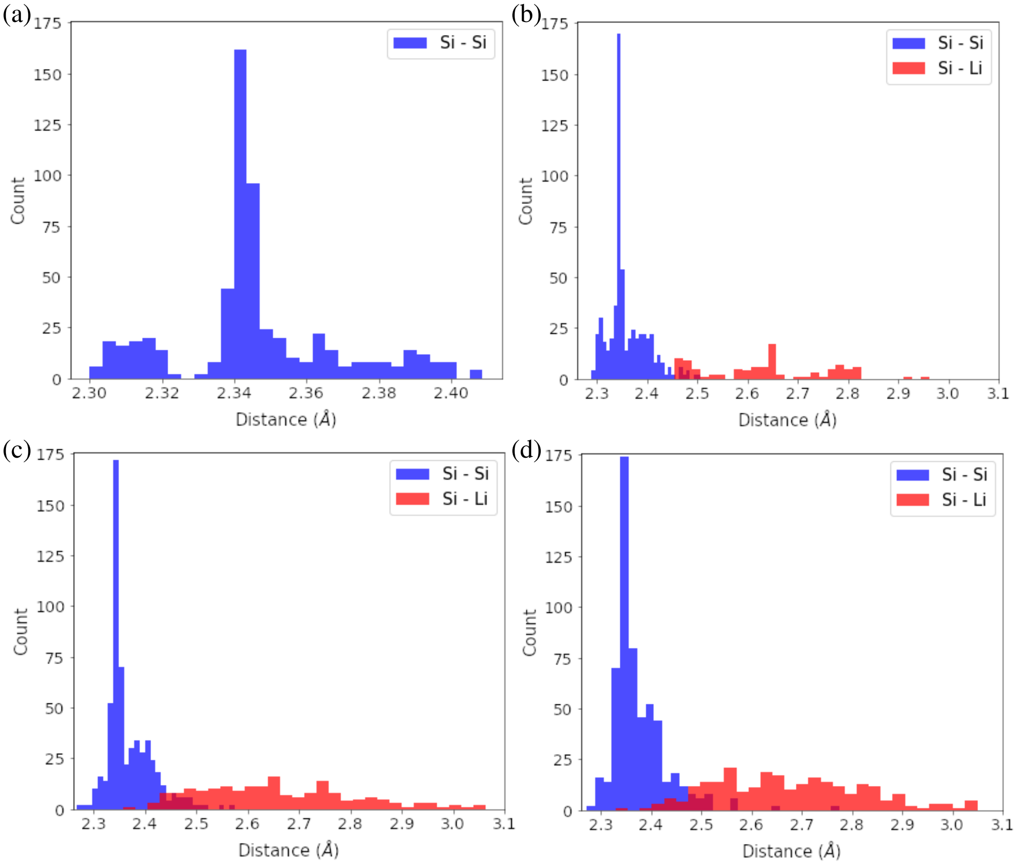
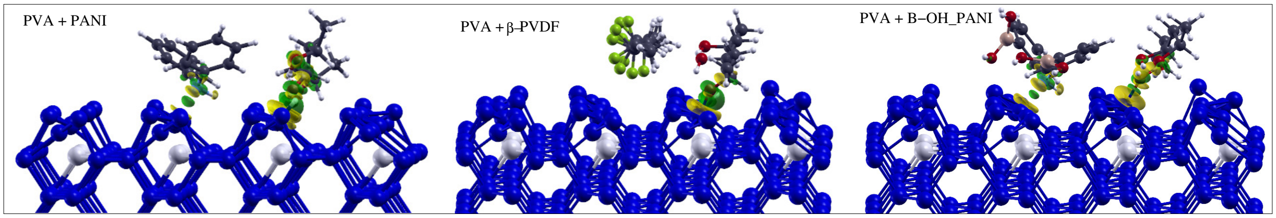


Figure 5S: Distribution of Si-Si and Si-Li nearest neighbour distances (Å) considering above five layers of (a) Si-111, (b) 10 Li-Si-111, (c) 20 Li-Si-111 and (d) 30 Li-Si-111.

(a) 8 Li–Si–110



(b) 24 Li–Si–110

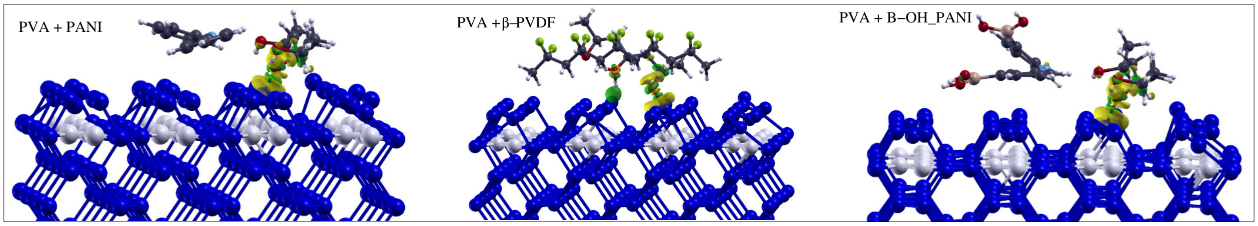


Figure 6S: Si(110): a) 8 Li and (b) 24 Li intercalated Si surface in the presence of co-binders with charge density difference ($\Delta\rho$) of PVA + PANI, PVA + β-PVDF and PVA + B-OH_PANI, with isosurface value 0.008.

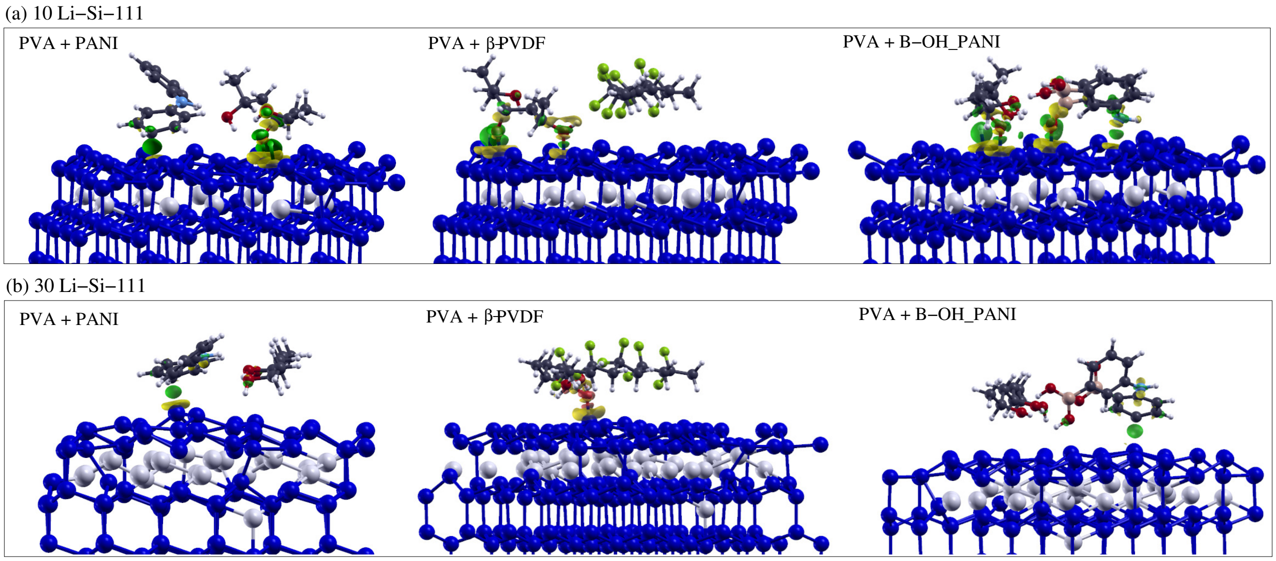


Figure 7S: Si(111): a) 10 Li and (b) 30 Li intercalated Si surface in the presence of co-binders with charge density difference ($\Delta\rho$) of PVA + PANI, PVA + β-PVDF and PVA + B-OH_PANI, with isosurface value 0.008.

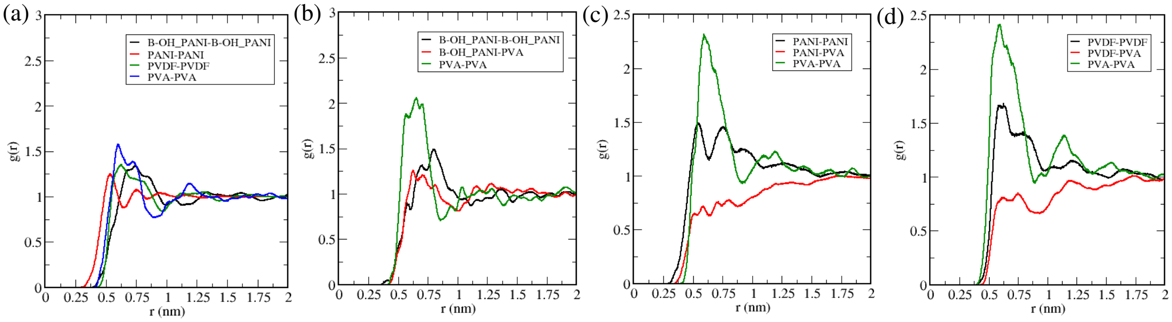


Figure 8S: Pair correlation function g(r) of the systems described previously in Table.??: (a) each curve represents one system, formed by one type of polymer. (b-d) co-binder configurations with PVA being common in all cases: (b) PVA+B-OH_PANI (c) PVA+PANI and (d) PVA+β-PVDF. For all cases, the reference for g(r) is the molecule center-of-mass, and the curve is the average over all the molecules in the system. g(r) of the co-binder is compared with their single binder model, which is marked in the legend of b-d accordingly.

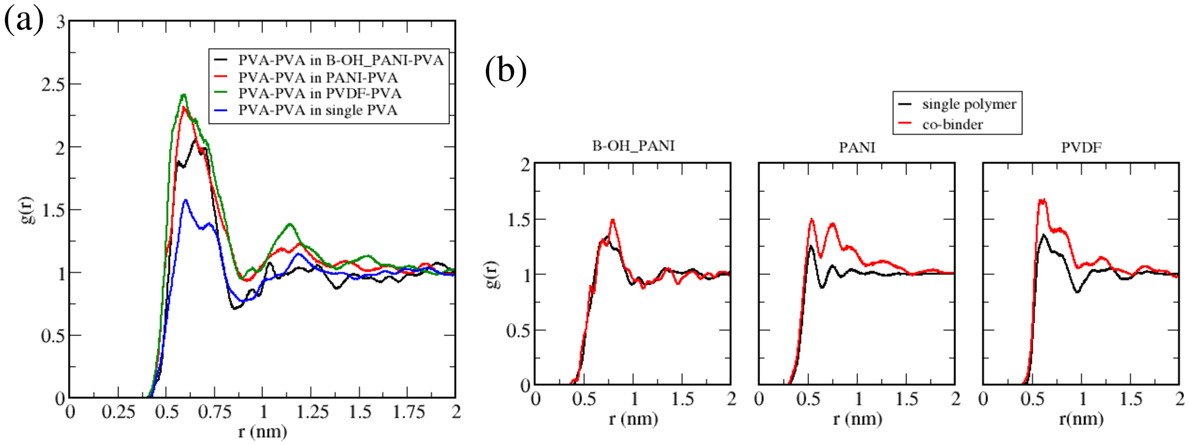


Figure 9S: Pair correlation function g(r) of the systems described previously. (a) Each curve represents one system, formed by one polymer. (b) comparison of single and co-binder configurations.

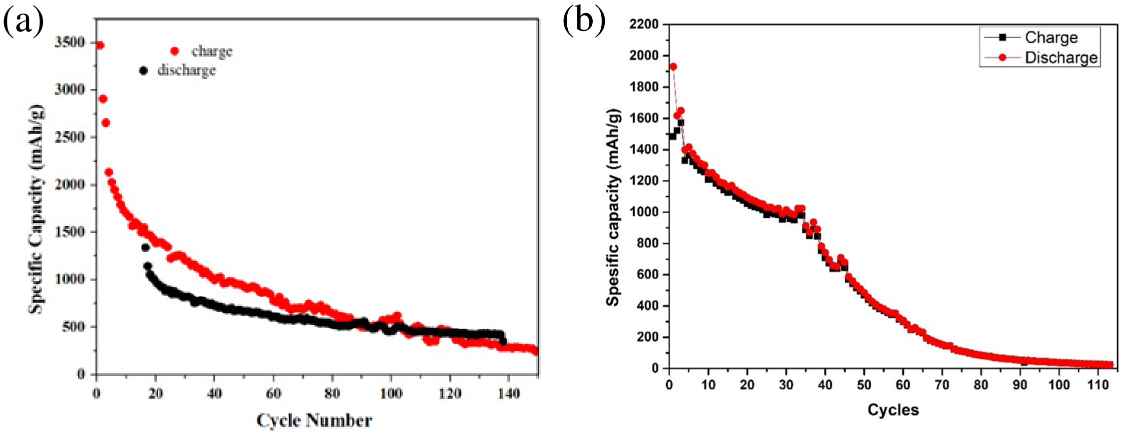


Figure 10S: (a) Cyclic performance of Si/B-OH_PANI-PVA cell at C/10 and, (b) Cyclic performance of Si/PVDF cell at C/10.

The practical application of the battery for B-OH_PANI based silicon anode has been provided in the following part:

Anode Electrode Preparation: The anode electrode slurry content has Si active material: PANI-PVA self-healing polymer (SHP) binder: conductive carbon additive (CB) as the ratio of 60:20:20. SHP binder was dispersed in water and then carbon additive and active material added respectively. This slurry was mixed with magnetic stirrer for 1h and then mixed with ultrasonic homogenizer for 1 hour to get a homogeneous slurry. The prepared slurry was laminated on copper foil by a doctor blade coated system and dried under the vacuum. The dried electrodes were cutted on 2032-coin cell size. The same procedure was applied for Si:PVDF:CB anode electrode for comparison.

Coin Cell Assembly: The electrodes were transferred to the glovebox after vacuumed in the chamber during the night. Li metal was used as a counter electrode and 1MLiPF6 in EC:DEC was used as the electrolyte.

Electrochemical tests: The cells were cycled between 1.2 V and 0.01 V. The galvanostatical test was performed at C/25 for 2 cycles and at C/10 for 100 cycles. The theoretical capacity of the silicon was assumed as 3500 mAh/g. Electrochemical impedance spectroscopy was applied at 100 kHz to 1 mHz. The Cyclic voltammetry curves are measured between 0.01 and 1.2 V at a scan rate of 0.1 mV/s.