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Modifying electron structure of FeCoNiZnCu high-entropy alloy with introduction of Cu for facilitating the catalytic effect in lithium sulfur batteries

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Calculations method

First-principles was employed to conduct density functional theory (DFT) calculation in generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) form.[1-3] The projected augmented wave (PAW) potentials were chosen to describe the ionic cores and valence electron was considered using a plane wave basis set with a kinetic energy cutoff of 450 eV. [4,5] Partial occupancies of the Kohn-Sham orbitals were allowed with the Gaussian smearing method and a width of 0.05 eV. For optimizing the geometry and lattice size, the Brillouin zone integration was performed with a 0.04 $Å^{-1}$ *k*-mesh Monkhorst-Pack sampling.[6] The self-consistent calculations applied a convergence energy threshold of 10^{-5} eV. The equilibrium geometries and lattice constants were optimized with maximum stress on each atom within 0.02 eV $Å^{-1}$. 15 Å vacuum layer was normally added to the surface to eliminate the artificial interactions between periodic images. The weak interaction was described by DFT+D3 method using empirical correction in Grimme's scheme.[7,8] Spin polarization method was adopted to describe the magnetic system. Isosurface level of charge density difference was set at 0.002 eV $Å^{-3}$. The adsorption energy was calculated as: $E_{ad} = E_{total} - E_{Li2S4} - E_{adsorbent}$, in which E_{total}, E_{Li2S4} and $E_{adsorbent}$ represent the total energy of Li_2S_4 on adsorbent, Li_2S_4 and adsorbent, respectively.[9]

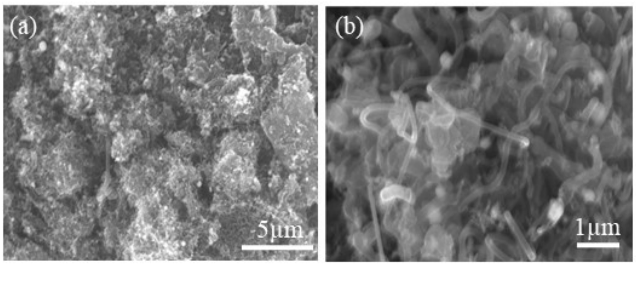

Fig. S1 SEM images of FeCoNiZnCu-NCNT: (a) low-magnification, (b) high-magnification

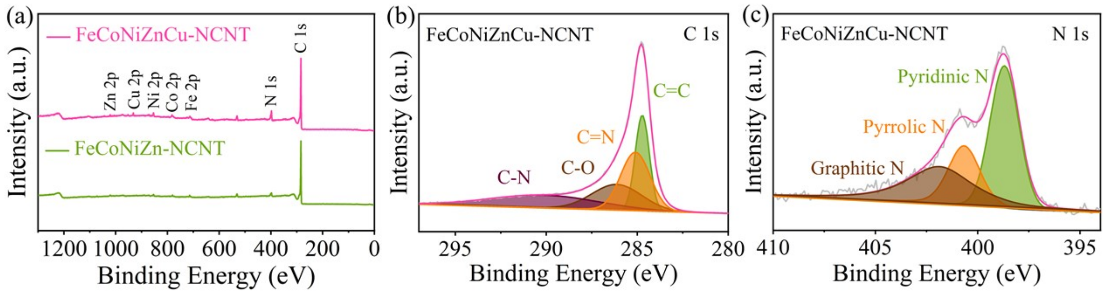

Fig. S2 (a) XPS full spectrum of FeCoNiZn-NCNT and FeCoNiZnCu-NCNT. XPS spectra of FeCoNiZnCu-NCNT: (b) C 1s, (c) N 1s

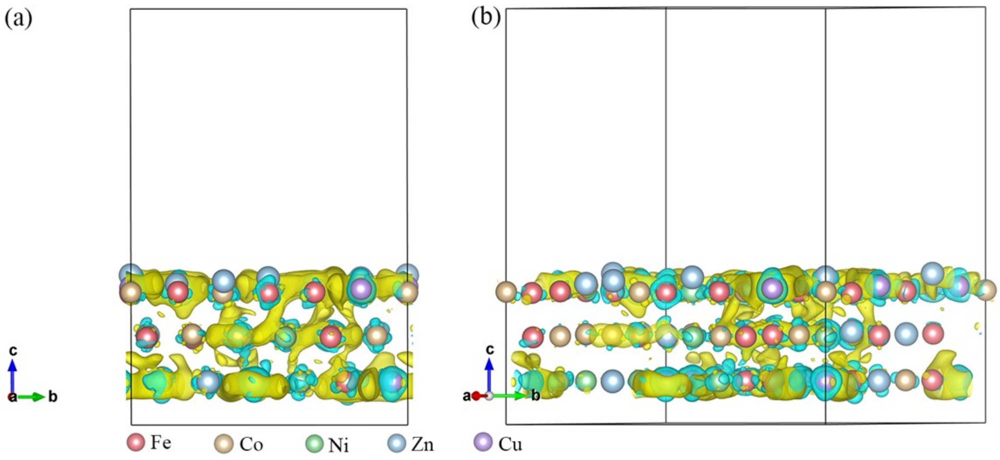

Fig. S3 Electron density difference of FeCoNiZnCu from different directions of (a) and (b)

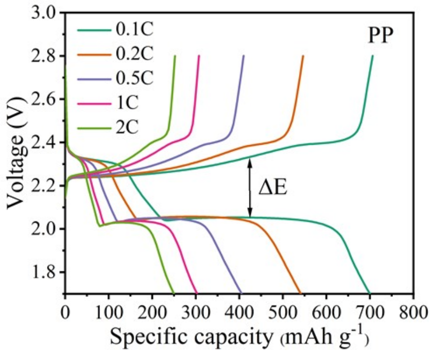

Fig. S4 First galvanostatic charge-discharge profiles of Li-S batteries with blank separator at different rates

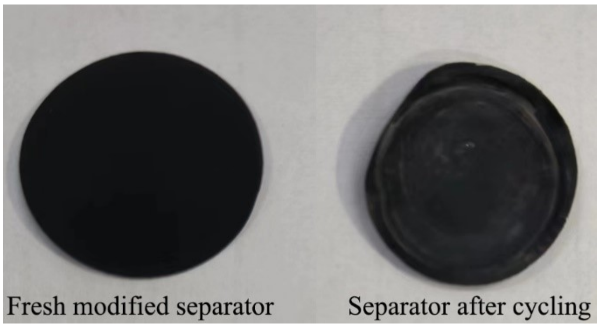

Fig. S5 Photos of modified separator before and after the battery was cycled

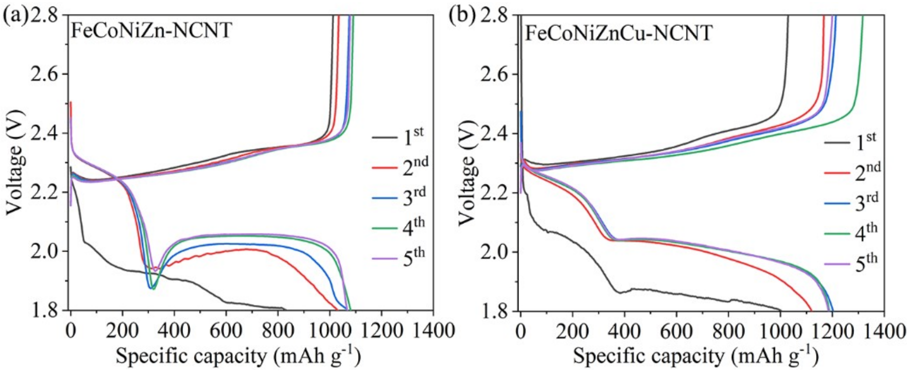

Fig. S6 Charge-discharge curves of the pouch cells at 0.1 C: (a) FeCoNiZn-NCNT, (b) FeCoNiZnCu-NCNT

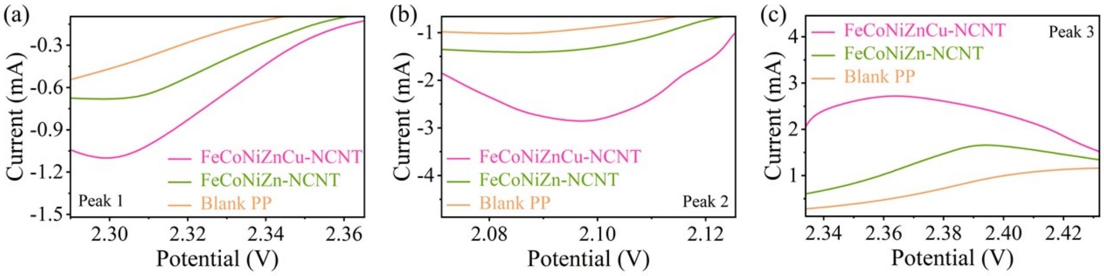

Fig. S7 Locally amplified CV curves of Fig. 5(a): (a) Peak 1, (b) Peak 2, (c) Peak 3

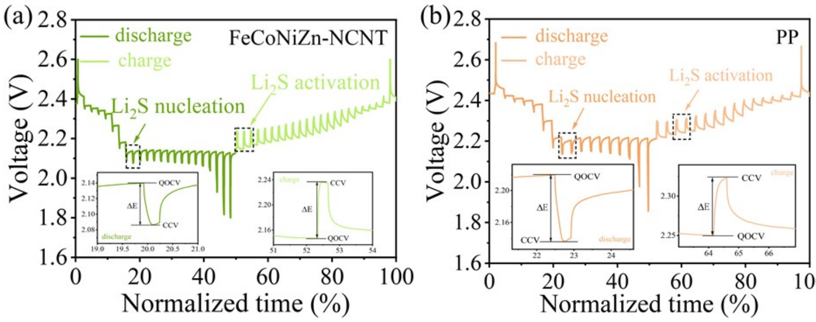

Fig. S8 GITT plots of LSBs with (a) FeCoNiZn-NCNT modified separator and (b) blank separator in the first discharge/charge process under the current density of 0.1 C

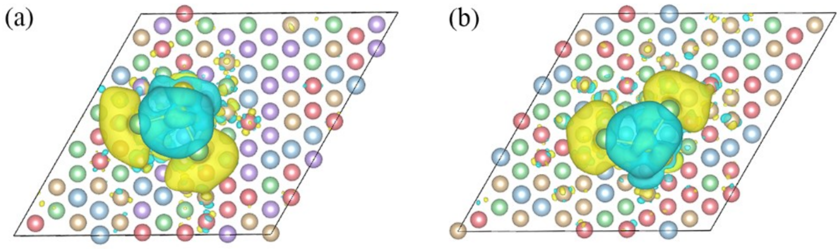

Fig. S9 Charge density difference diagram of Li_2S_4 adsorbed on different catalyst surfaces, in which charge accumulation is represented by yellow region, charge depletion is represented by cyan region

Table S1 Comparison of electrochemical performance to other papers related to HEA catalysts

Materials	Specific capacity at 0.1C (mAh g^{-1})	Capacity retention	Specific capacity at 1C (mAh g^{-1})	Decay rate	Ref.
FeCoNiZnCu	1301.6	75%	820.9 (1C)	0.07% (600 cycles)	This work
FeCoNiCuMn	1494.1	70.7%	740.1 (1C)	0.05% (970 cycles)	Ref.[10]
FeCoNiMnZn	About 1200 (0.2C)	-	816 (2C)	0.03% (500 cycles)	Ref.[11]
MgCrMnFeCoNi	1301.5	-	752.2 (2C)	-	Ref.[12]

Table S2 Comparison of adsorption energy of catalysts for Li_2S_4 to other papers

Materials	LiPSs	Adsorption energy	Ref.
FeCoNiZn	Li_2S_4	-7.44 eV	This work
Defective $MoSe_2$	Li_2S_4	-6.84 eV	Ref.[13]
CoP	Li_2S_6	-2.6 eV	Ref.[14]
SnO_2	Li_2S_4	-5.46 eV	Ref.[15]
$CoNiO_2$	Li_2S_6	-5.69 eV	Ref.[16]
$CoNiO_2/Co_4N$		-4.48 eV	
$Ni_{0.2}Mo_{0.8}N$	Li_2S_4	-2.01 eV	Ref.[17]
$Cu_{0.1}Co_{0.9}P$	Li_2S_6	-5.58 eV	Ref.[18]
$P\subset NiTe_{2-x}$	Li_2S_6	-5.26 eV	Ref.[19]

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