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Supplementary information: A concept of dual-salt polyvalent-metal storage battery

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It would be interesting to know to what extent the energy density is retained or improved by substituting a non-noble polyvalent metal for graphite negative electrode of conventional lithium ion batteries (LIBs). In general, the accurate energy density calculation is difficult, because there are many factors to be considered for the calculation (e.g., the weights of metallic current collectors, separator, solvent etc, other than the two electrodes and electrolyte solute). For the dual-salt Daniel type batteries, we have considered the case where magnesium is used as a negative electrode, on the assumption that small amount of electrolyte (or solvent) is only required by using a saturated electrolyte with precipitated salts. Here we consider two kinds of the anion A, Cl^- and BF_4^-, for LiA and MgA_2 salts. SI Table I compares the expected capacities, *Emf*, energy densities of the conventional rocking-chair batteries and dual-salt Daniel type batteries. In this calculation, we have taken up the three intercalation-type positive electrode materials ($LiCoO_2$, $LiFePO_4$, and $LiMn_2O_4$), two conversion-type positive electrode materials (FeF_3 and CoF_3), and also $Mg_2Mo_6S_8$ positive electrode materials[4] for a rocking-chair type Mg battery. The energy densities of the dual-salt Daniel type batteries are found to be almost comparable to the LIBs with a graphite negative electrode when using intercalation-type positive electrode materials on the assumption that LiCl salt, existing as a precipitates in the small amount of saturated electrolyte, works as a Li^+ ion reservoir. The overall energy density (E_{P+N}) can be kept at a high value since the energy density of Mg (E_N) is significantly high; however, if we take a count of the electrolyte amount, the energy density is inevitably lowered.

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SI Table I: Theoretical, actual capacities and expected energy densities for various combinations of positive and negative electrodes (PE and NE). The value of availability means the amount of Li (or Mg) that can be used without the decomposition of the active materials, and C_{the} and C_{act} mean the theoretical and actual ($C_{\mathrm{act}} = xC_{\mathrm{the}}$) capacities. E_{P} and E_{N} (given by $C_{\mathrm{act}} \times$ *Emf*) indicate the expected energy densities by using only positive electrode material, only negative electrode material, respectively, and $E_{\mathrm{P+N}}$ is the overall energy density of both electrode materials, where the underlined materials are defined as a positive active material for the calculation of E_{P}. Note that the amount of electrolyte (or solvent) is not considered for the energy-density calculations. The *Emf* values are estimated on the basis of the data in literature.[20] The theoretical capacities of graphite (372 mAh g^{-1}) and Mg (2234 mAh g^{-1}) were used for the estimation of the energy densities.

Capacity and energy density	x	C_{the} mAh/g	C_{act} mAh/g	*Emf* V	E_{P} mWh/g	E_{N} mWh/g	$E_{\mathrm{P+N}}$ mWh/g
Rocking-chair type							
Intercalation reaction							
$Li_{1-x}CoO_2 + xLiC_6 = \underline{LiCoO_2} + 6xC$	0.6	274	164	3.7	608	1378	422
$Li_{1-x}FePO_4 + xLiC_6 = \underline{LiFePO_4} + 6xC$	1.0	170	170	3.1	527	1154	362
$Li_{1-x}Mn_2O_4 + xLiC_6 = \underline{LiMn_2O_4} + 6xC$	0.8	148	119	3.5	415	1303	315
$(1/2)Mg_{2(1-x)}Mo_6S_8 + xMg = (1/2)\underline{Mg_2Mo_6S_8} + 0$	1.0	122	122	1.2	146	2681	146
Conversion reaction							
$FeF_3 + 3LiC_6 = \underline{Fe + 3LiF} + 18C$	-	602	602	2.6	1565	968	598
$CoF_3 + 3LiC_6 = \underline{Co + 3LiF} + 18C$	-	588	588	3.3	1941	1229	752
Dual-salt Daniel type							
Intercalation reaction with LiCl							
$\underline{Li_{1-x}CoO_2 + xLiCl} + (1/2)xMg = LiCoO_2 + (1/2)xMgCl_2$	0.6	225	135	3.3	445	7372	420
$\underline{Li_{1-x}FePO_4 + xLiCl} + (1/2)xMg = LiFePO_4 + (1/2)xMgCl_2$	1.0	139	139	2.7	375	6031	353
$\underline{Li_{1-x}Mn_2O_4 + xLiCl} + (1/2)xMg = LiMn_2O_4 + (1/2)xMgCl_2$	0.8	128	103	3.1	318	6925	304
Intercalation reaction with $LiBF_4$							
$\underline{Li_{1-x}CoO_2 + xLiBF_4} + (1/2)xMg = LiCoO_2 + (1/2)xMg(BF_4)_2$	0.6	179	107	3.3	354	7372	338
$\underline{Li_{1-x}FePO_4 + xLiBF_4} + (1/2)xMg = LiFePO_4 + (1/2)xMg(BF_4)_2$	1.0	110	110	2.7	296	6031	282
$\underline{Li_{1-x}Mn_2O_4 + xLiBF_4} + (1/2)xMg = LiMn_2O_4 + (1/2)xMg(BF_4)_2$	0.8	107	86	3.1	266	6925	256
Conversion reaction with LiCl							
$\underline{FeF_3 + 3LiCl} + (3/2)Mg = 3LiF + Fe + (3/2)MgCl_2$	-	335	335	2.2	737	4914	641
$\underline{CoF_3 + 3LiCl} + (3/2)Mg = 3LiF + Co + (3/2)MgCl_2$	-	331	331	2.9	959	6478	835
Conversion reaction with $LiBF_4$							
$\underline{FeF_3 + 3LiBF_4} + (3/2)Mg = 3LiF + Fe + (3/2)Mg(BF_4)_2$	-	204	204	2.2	449	4914	411
$\underline{CoF_3 + 3LiBF_4} + (3/2)Mg = 3LiF + Co + (3/2)Mg(BF_4)_2$	-	202	202	2.9	587	6478	538