Hybrid Aqueous Electrolyte for High Energy Density Dual-ion Battery

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(高エネルギー密度デュアルイオン電池のためのハイブリッド水系電解液)
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論　文　内　容　の　要　旨
Thesis Summary

DIBs, a novel battery system beyond the conventional LIBs, have received great attention in the past several years. The anion intercalation reaction in graphite achieves a high operating voltage and is an ideal cathode candidate for high energy batteries, however, additional advancements are required to achieve for practical application. Concentrated aqueous electrolytes solved the solubility limitation of supporting salts in organic solvent, providing technical superiority in high-energy DIBs development with new chemistries and greater availability of materials. However, the development of aqueous DIBs is still at a very early stage and the aqueous electrolyte systems with adequate stability is still strongly required. In this study, stable aqueous electrolytes which suits to use in DIBs system for increasing energy density are investigated, in particular, hybrid aqueous electrolyte with high concentration of LiFSI-LiTFSI is focused.

In Chapter 2, the effects of the concentrated hybrid acetonitrile (AN)-water electrolytes on the electrochemical stability window and electrochemical performance of KS6/AC dual-ion batteries are investigated. In particular, 20 mol kg^{-1} W1A1 (20 mol 3LiTFSI/1LiFSI (molar ratio) dissolved in 1kg mixture of $1H_2O$/1AN (molar ratio)) electrolyte was optimized compositions from the wide electrochemical stability windows of 3.48 V and proper viscosity and conductivity. By series of spectroscopic analysis, it is revealed that stronger solvation structure formed by interaction of solvent molecules, Li^+ and anion, resulting in a high oxidative tolerance. This electrolyte is applied to a KS6/AC half-cell, which achieves an average coulomb efficiency of 85% and discharge capacity of 86 mAh g^{-1} at initial cycle in 0–3.25 V. Furthermore, the energy density of KS6/AC cell is estimated to be 170 Wh kg^{-1} which is almost the same level with that of the current LIBs and much larger than the conventional dual-ion batteries.

In chapter 3, addition of tetraglyme (G4) to aqueous electrolytes dissolving 37 mol kg^{-1} LiFSI–LiTFSI (9:1, molar ratio) are studied on the electrochemical stability window and electrochemical performance of KS6/AC DIB half-cell. It is found that this hybrid G4-water electrolyte highly effective to expand electrochemical stability window and prevent hydrogen evolution reaction, i.e., a voltage window of 3.3 V and suppressed hydrogen evolution reaction potential to −1.05 V vs. Ag/AgCl without decreasing oxygen evolution reaction potential. This improvement in stability of aqueous electrolyte by G4 addition is explained by the strong solvation of G4 to Li^+ and the strong solvated ion pair $[Li(G4)_x(H_2O)_y]^+$. 37 mol kg^{-1} G2W8 (37 mol 9LiFSI-1LiTFSI (molar ratio) was dissolved into 1 kg mixture of G4 and water (weight ratio, 2:8)) electrolyte is applied in a KS6/AC dual-ion cell exhibited a discharge capacity of 63 mAh g^{-1} at the

initial cycle and an average coulombic efficiency of 90% and 40 mAh g^{-1} was sustained over 300 cycles. Since energy density of dual-ion batteries increases with increasing concentration of supporting salt, 37 mol kg^{-1} 9LiFSI–1LiTFSI hybrid G4 water electrolyte is highly promising as electrolyte for aqueous dual-ion batteries with high energy density, low cost, and high safety.

In chapter 4, change in solvation cluster by addition of tetraglyme are investigated from activation energy of intercalation of Li^+ and anions. Electrochemical impedance spectra (EIS) measurement is firstly applied to estimate anion intercalation activation energy, which revealed formed $Li(G4)^+$ complexes greatly increased activation energy of Li^+ intercalation, however, decreased activation energy of anions intercalation process. The increased capacity of KS6/AC half-cell by addition of G4 may be explained by change of contact ion pair structure which means anion freer. The stability of hybrid G4 water electrolytes are further studied by plastic-bag KS6/Mo_6S_8 cells with charge-discharge cycles and impedance measurement. Increased performance can be assigned to the suppression of electrolyte decomposition and carbonaceous electrode oxidation. These results and the proposed concept in this work provides a new direction for electrolytes engineering.

In chapter 5, a new $FeNbO_4$-$MoNb_{12}O_{33}$ composite is synthesized to use as anode material to enhance discharge capacity and stability in hybrid G4-water electrolyte system. EIS and GITT measurements reveal $FeNbO_4$ formed in $MoNb_{12}O_{33}$ could effectively decrease energy barrier of Li^+ intercalation process and promote Li^+ diffusion coefficient in $MoNb_{12}O_{33}$, delivering excellent electrochemical performance to this niobate-based composites. Fe0.5-MNO composite/AC half-cell using hybrid G4-water electrolyte performs a discharge capacity of 100 mAh g^{-1} at initial cycle and high average coulombic efficiency of 98% over 200 cycles in a voltage range of -1.3~0 V vs. Ag/AgCl, which indicates Fe0.5-MNO composite as anode possess great hydrogen evolution reaction (HER) inhibition ability. The full cell using Fe0.5-MNO, brings excellent long cyclic stability over 1000 cycles, which shows discharge capacity of 61 mAh g^{-1} at initial cycle, 36 mAh g^{-1} at 1000th cycle and average coulombic efficiency of 87% over 1000 cycles. Therefore, the niobate-based composites would be an excellent anode material in aqueous systems, delivering a more stable, high operating voltage and performance aqueous dual-ion batteries.