Practicality and electrochemistry of acetate water-in-salt electrolyte (WISE) for zinc battery cycling

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Background

Water-in-salt electrolyte (WISE) receives great attention recently as a method to boost the voltage stability of aqueous electrolyte batteries. Despite the many publications, practical or realistic battery testing is missing from the literature. Here we test potassium acetate (KAc) WISE with a practical cell design and commercially relevant coulombic areal capacity and current density. We also test the prevailing cell design and commercially recently as a method to boost the voltage stability of aqueous electrolyte batteries. Here we show that WiSE do not gain voltage with a practical electrolyte blocking layers.  Zinc plating/deplating in WISE occurs with a ~20x lower Tafel slope than in 25% KOH, likely also due to blocking layers.

Electrochemistry of K-Acetate WISE Electrolyte

Hydrogen evolution in KAc WiSE (Fig 3) shows a ~100 mV shift of onset and is 40x lower than in 25% KOH, and although the mechanism for this reduction is unknown a leading hypothesis is that higher OH- concentration speeds up the rate-limiting step of converting adsorbed H to H2. Oxygen evolution in KAc WISE electrolyte (Fig 3) shows a 400 mV shift of onset voltage but this shift can be eliminated by stirring (RDE rotation), thus the voltage-stability mechanism seems to be a SEI-like blocking layer. Zinc plating/deplating in WISE occurs with a ~20x lower Tafel slope than in 25% KOH, likely also due to blocking layers.

Fig. 1. Molecular model of 1 molal KAc vs. 27 m KAc WiSE, and the resulting capacity and current density. We also test the prevailing cell design and commercially recently as a method to boost the voltage stability of aqueous electrolyte batteries. Here we show that WiSE do not gain voltage with a practical electrolyte blocking layers. Zinc plating/deplating in WISE occurs with a ~20x lower Tafel slope than in 25% KOH, likely also due to blocking layers.

Fig. 2. Zinc plating/deplating in 27 mKAc WISE.

Fig. 3. Hydrogen evolution reaction via decomposition, 27 mKAc WiSE vs. traditional electrolyte (25% KOH).

Fig. 4. Oxygen evolution reaction via electrolyte decomposition, 27 mKAc WiSE vs. 25% KOH.

Fig. 5. Zn plating/deplating in 27 mKAc WISE.

Fig. 6. WISE performs poorly with an industrial cell design and practical coulombic areal capacity.

Testing of KAc WISE in practical cell design and industrial coulombic areal capacity (Fig 6 and Fig 7) shows poor performance due to excessive overvoltage from the WISE, due to slow ionic transfer and is the only formula that cycles well in our testing. Only stripped solutions show capability to cycle.

Fig. 7. Overvoltage and coulombic efficiency in (a), (b), and (c) show improvement with added H2O. Photographs of dendrite formation in (c), (d), (e), (f) show shorter dendrites in KAc WISE.

Conclusions

Electrolyte voltage stability in WISE is improved compared to traditional KOH electrolyte, but is not controlled by H2O activity as claimed often in literature. Rather, reaction kinetics and SEI layers control voltage stability. Zn plating/deplating is too slow in nominal KAc WISE for commercially-relevant current density. Dilution of WISE improves mass transfer but reduces voltage stability. Zn dendrites are reduced in KAc WISE. Future research aims to improve Zn plating/deplating in KAc WISE without reducing voltage-stability.

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References


Fig. 8. Zn Ac solubility is boosted by interaction with K Ac.