

Hydroxide ion conductive polymer electrolytes for electrochemical supercapacitors

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INTRODUCTION

Alkaline electrolytes, especially KOH, have been extensively applied in electrochemical supercapacitors (ECs) including double layer and pseudocapacitive electrodes in symmetric or asymmetric configurations [1-3]. To develop thin and flexible solid ECs, alkaline-based polymer electrolytes are necessary for serving as OH^- conductor and separator. Extensive studies have been performed on KOH-polyvinyl alcohol (PVA) system [4]. However, KOH-PVA gel film showed poor adhesion due to the slippery nature of alkaline solution. This leads to poor long term stability of the EC devices.

In this study, our objectives are: (a) to investigate and select a suitable alternative to KOH from quaternary ammonium salts with different cations, namely tetramethylammonium hydroxide (TMAOH), tetraethylammonium hydroxide (TEAOH), and tetrabutylammonium hydroxide (TBAOH) for equal or better ionic conductivity and capacitance; and (b) to develop and characterize the performance of the selected quaternary ammonium salt-PVA polymer electrolytes.

EXPERIMENTAL

Aqueous electrolytes based on KOH and quaternary ammonium salts were prepared in different concentrations. A standard test vehicle was constructed using two smooth nickel foils (Ni) as electrodes. For the polymer electrolytes, aqueous polymer electrolyte precursor solutions with a mixture of PVA and quaternary ammonium salts or KOH were prepared with same salt to polymer molar ratio. Ni was used as metallic electrodes. The electrode area was 1 cm^2 . The devices were characterized using cyclic voltammetry (CV) and ac impedance spectroscopy. All tests were performed in ambient condition unless otherwise specified.

RESULTS AND DISCUSSION

Ionic conductivity of the three quaternary ammonium salts and KOH were first compared in the liquid state (Fig. 1). For all electrolytes, the conductivity increased with concentration. TMAOH and TEAOH showed comparable conductivity values to KOH. Due to the relative large cation size of TBAOH, it exhibited the lowest ionic conductivity. Figure 2 shows the overlaid CVs of the four liquid cells at 1M concentration. At an ultra-high scan rate of $5,000 \text{ Vs}^{-1}$, both TMAOH and TEAOH-based cells could deliver comparable capacitance to the KOH cell. Due to the lower dissociation of TBAOH and its lower conductivity, it had the lowest capacitance.

TEAOH was selected to prepare TEAOH-PVA polymer electrolytes. Fig. 3 shows a CV overlay of two pristine polymer electrolyte-based cells (TEAOH-PVA and KOH-PVA). For a direct comparison, same salt to polymer molar ratio was controlled for both TEAOH-PVA and KOH-PVA in the precursor solutions. Both cells showed similar capacitance at 1 Vs^{-1} . More details

about conductivity and long term stability of TEAOH-PVA electrolytes will be discussed. In addition, structural characterizations of TEAOH-PVA will also be presented.

REFERENCES

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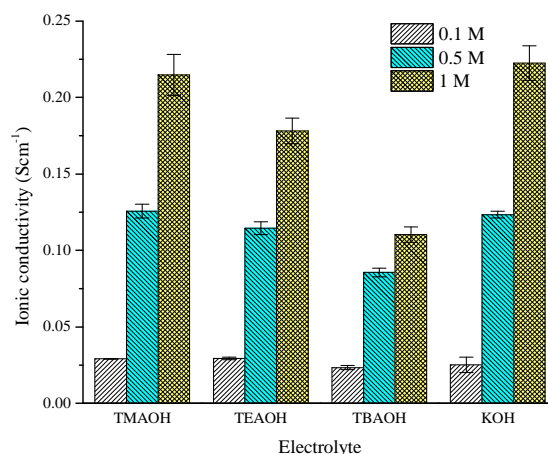


Fig. 1 – Comparison of ionic conductivity of liquid TMAOH, TEAOH, TBAOH, and KOH in different concentrations at 298 K

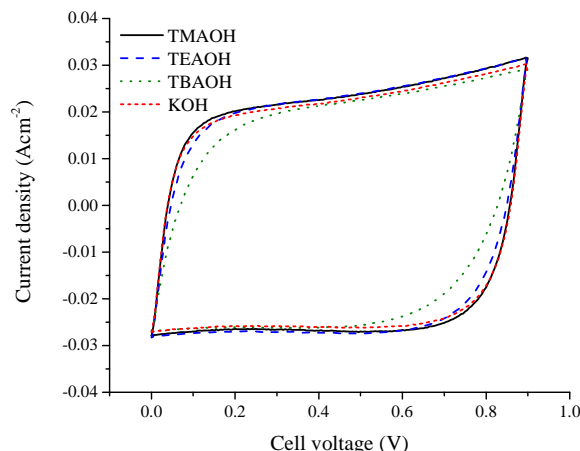


Fig. 2 – CVs of liquid TMAOH, TEAOH, TBAOH, and KOH metallic cells all in 1M concentration at 298 K (scan rate = $5,000 \text{ Vs}^{-1}$)

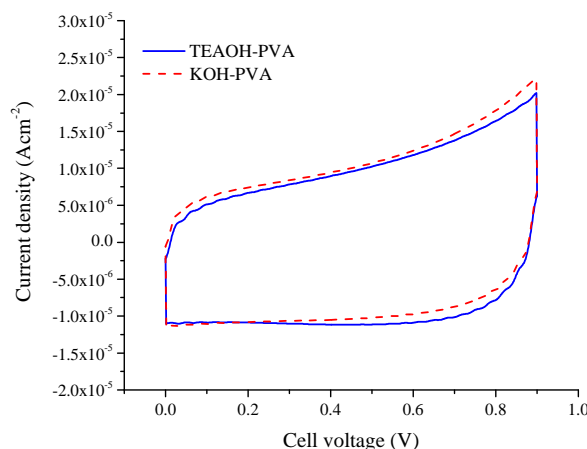


Fig. 3 – CVs of polymer electrolyte-based ECs using TEAOH-PVA and KOH-PVA at the ambient (scan rate = 1 Vs^{-1})