Eumelanin as biologically derived cathodes for aqueous sodium ion energy storage

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Statement of Purpose: Biodegradable electronics presents an emerging paradigm in biomedical applications by exhibiting various advantages afforded by electronically active devices systems and obviating issues with chronic implants. Energy harvesting strategies that are compatible with the envisioned operation of transient devices remain an unmet challenge for biodegradable electronics. Eumelanins are broad class of pigments that can be found in many organisms. Eumelanins exhibit exceptional in vivo and in vitro biodegradability via free radical degradation mechanism. Eumelanins exhibit hydration dependent electronic ionic conduction via self-doping. Eulemanins exhibit unique chemical signatures such as catechols, pendant amine, and carboxylates that allow reversible binding of monovalent and divalent cation. Herein, we present the utility of eumelanin pigments as cathode materials in aqueous sodium ion charge storage devices.

Methods: Natural (extracted from *Sepia Officinalis*) (NatMel) and synthetic (SynMel) eumelanin pigments were used as cathode materials by incorporating with silver nanowire (AgNW). Sodium titanium phosphate (STP, $NaTi_2(PO_4)_3$) was prepared by solid state sintering using precursors of NaH_2PO_4 H_2O, TiO_2, and $(NH_4)_2HPO_4$ with molar ratio of 1:2:2 mixed with 5 wt% graphite. Galvanostatic half-cell discharges were measured in aqueous electrolytes of 1M Na_2SO_4 with three-electrode cell configuration. Potentiostat-galvanostat was used to measure cyclic voltammograms (CV), galvanostatic half-cell and full cell discharge profiles. Sheet resistances of the composites were measured using a four-point probe configuration with probe station with gold microwire contacts and two source meters. The cross-sectional morphologies of eumelanin/AgNW cathodes were characterized by environmental scanning electron microscopy (SEM). Raman and FT-IR spectra were recorded to examine the molecular structure changes before and after discharges.

Results: The bulk electron conductivities of eumelanins in dehydrated states were increased by incorporating with AgNW. Measured sheet resistances as low as 4.97 ± 1.45 and 6.44 ± 1.73 $\Omega\ \square^{-1}$ were observed for NatMel and SynMel composites, respectively. The single cathode peak from CV corresponds to the loading of Na+ into melanin during reduction. The peak current proportionally increased with the concentration of AgNW. These data suggest that the increase of AgNW density promoted the charge collection by increasing accessibility of redox-active functional groups in eumelanins. This is in a good agreement with the homogeneous morphology of eumelanin/AgNW composite shown in SEM in Fig. 1(b). Galvanostatic full cell potential profile of NatMel cathode and STP anode is shown in Fig. 1(c) with initial potential of 0.9 V and stabilized at 0.5 V. The specific charge storage capacity of full cells increases monotonically with increased AgNW loading. Due to different microstructure and chemical composition of NatMel and SynMel, discrete potential plateaus were observed from NatMel while SynMel exhibited more gradual potential reduction. Unlike SynMel, Na^+ association with NatMel cathodes occurs at two discrete potentials, which leads to alter the molecular structure of NatMel. Spectroscopic analysis suggests that the evolution of spectroscopic signatures is consistent with partial exfoliation of molecular structures, which further causes increased exposure of aromatic amines in NatMel.

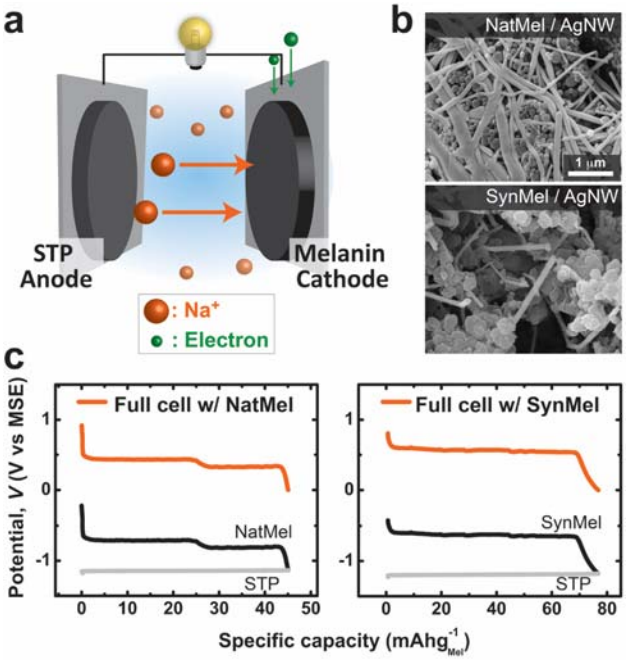

Fig. 1. (a) Schematic illustration of full cell discharge configuration composed of STP anode and melanin cathode. Microstructure of NatMel/AgNW and SynMel/AgNW (30 wt%) composites with homogeneous distribution are shown in (b). Full cell potential profiles of NatMel/AgNW and SynMel/AgNW are shown in (c).

Conclusions: Eumelanin pigments exhibit unique redox properties by allowing reversible cation exchange and are potentially advantageous as biologically-derived charge storage materials for next generation transient electronics devices and biomedical implants.

References:

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