THE JOURNAL OF PHYSICAL CHEMISTRY C
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
pubs.acs.org/JPCC

Article

Wide Electrochemical Stability Window of Boron-Doped Microcrystalline Diamond Electrode in $NaNO_3$ Water-in-Salt Electrolytes

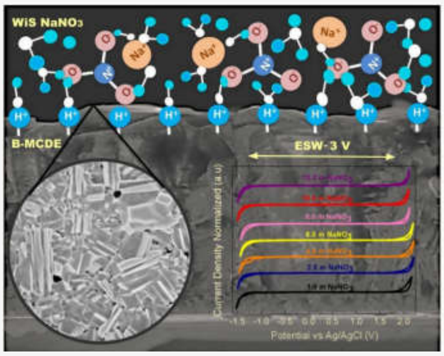
Oksana Gutsul,* Rene Pfeifer, Ondrej Szabo, Dhananjay K. Sharma, Jaroslav Kuliček, Nirmal Kumar, Alexander Kromka,* and Bohuslav Rezek

Cite This: https://doi.org/10.1021/acs.jpcc.5c00414

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Expanding the electrochemical stability window (ESW) of aqueous electrolytes can contribute to the high energy density of electrochemical energy-storage devices and supercapacitors. Here, we demonstrate a unique electrochemical interaction in two- and three-electrode configurations of sodium nitrate ($NaNO_3$) water-in-salt (WiS) electrolyte in a wide range of concentrations (1−12 m) with an electrode made of boron-doped microcrystalline diamond (B-MCDE, grain size ~1 mm) deposited by a microwave plasma chemical vapor deposition process. Compared to the commercial glassy carbon electrode (C-GCE), the ESW reached ~3 V. In the frequency range of 10 mHz−100 kHz, the B-MCDE also demonstrated better conductive (down to R_{ct} of 50 Ω) and capacitive (up to C_{dl} 3.2 μF) properties compared to the C-GCE for all WiS electrolyte concentrations, where the appropriate equivalent circuit was identified. The best performance was obtained for the 8 m WiS concentration at neutral pH and room temperature, while the 12 m WiS was unstable, as confirmed by Raman spectroscopy. The expanded ESW and superior performance of B-MCDE are explained by its high-quality material properties and nanostructured surface (almost nanoporous, feature size <100 nm) formed in the WiS electrolyte. The results reveal that with a well-controlled quality, boron-doped diamond electrodes are advantageous for WiS supercapacitors.



1. INTRODUCTION

Modern energy-storage devices require increased energy density and power.[1,2] At the same time, it is necessary to ensure high reliability and low cost. Electrical double-layer capacitors, so-called SCs, are important electrochemical energy-storage devices due to their fast charging and discharging capabilities and ultralong lifetime.[3,4] However, the low energy density remains a significant problem for SCs.[5,6] One of the simplest yet highly effective approaches to increasing the energy density is using high-voltage organic electrolytes, which are currently used for commercial 2.3−3.0 V SCs.[7] However, organic electrolytes' main problems are flammability and volatility.[8] Some pure ionic liquids used as electrolytes at room temperature provide the operating voltage of SCs up to 4.0 V, but they have high viscosity, which seriously degrades the ion transport, leading to slow energy uptake of SCs.[3] In particular, organic electrolytes and ionic liquids are quite sensitive to moisture, which requires additional complex manufacturing processes.[9] Aqueous electrolytes, in general, can be used as an alternative to solve the problems listed above. Aqueous electrolytes are available, cheaper, and environmentally friendly.[9] However, the electrochemical stability windows (ESWs) of aqueous electrolytes are significantly narrower than those of organic electrolytes due to the low decomposition voltage of pure water of ~1.23 V.[8,10]

In contrast to low-concentration electrolytes, highly concentrated electrolytes exhibit extraordinary functionality. Water-in-salt (WiS) electrolytes are a new class of super-concentrated systems.[3,4,6,7,11−16] They exhibit extremely broad ESWs due to the significantly reduced water content and effective confinement of the chemical activity of the water molecules. The first WiS electrolyte was obtained by dissolving LiTFSI in water with a high salt-to-water molar ratio of 1/2.6 (i.e., 21 m (mol kg^{-1})), which demonstrated a wide ESW of 3.0 V when using stainless steel electrodes.[3] In this paper, Guo et al. showed that increasing the salt concentration allows the ESW to be broadened, enabling high-voltage electrodes to obtain significantly higher energy densities. Compared to the LiTFSI electrolyte, $NaNO_3$ has the advantage of higher conductivity, lower viscosity, and lower commercial price.[3] WiS $NaNO_3$ electrolyte is optimal among those using WiS electrolytes with higher solubility, such as 17 m $NaClO_4$, 21 m

Received: January 18, 2025
Revised: April 14, 2025
Accepted: April 29, 2025

https://doi.org/10.1021/acs.jpcc.5c00414
J. Phys. Chem. C XXXX, XXX, XXX−XXX