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Topic B

B13

Comparative Study of Mixed Nickel-Manganese Hydroxides/Oxides and Phosphates as Electrodes for Hybrid Supercapacitors

L. Soserov[1], D. Marinova[2], V. Koleva[2], A. Stoyanova[1] and R. Stoyanova[2]

[1] *Institute of Electrochemistry and Energy Systems "Acad. Evgeni Budevski", Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

[2] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

E-mail: manasieva@svr.igic.bas.bg

Keywords: hybrid supercapacitors, Ni/Mn oxides, hydroxides and phosphates, synergetic effect, capacitance performance, alkaline electrolyte.

Hybrid supercapacitors with the composite electrode materials display high energy density at the expense of the reduced cycle stability. In the last few years nanostructured transition metal oxides, hydroxides and phosphates as a new type of energy storage materials have widely attracted attention. Herein, we provide data on the electrochemical performance of hybrid supercapacitors based on mixed nickel/manganese oxides, hydroxides and phosphates in the form of structured and multiphase composites.

Mixed nickel-manganese oxides with ilmenite and spinel structures ($NiMnO_3$ and $Ni_{1.5}Mn_{1.5}O_4$), hydroxides with layered structures (β-$Ni_{1/2}Mn_{1/2}(OH)_2$), and phosphates with olivine and maricite structures ($LiNi_{1/2}Mn_{1/2}PO_4$ and $NaNi_{1/2}Mn_{1/2}PO_4$), obtained from different precursors, have been investigated in a mixed alkaline electrolyte (KOH with LiOH). The electrochemical performances of composites electrodes are determined by galvanostatic charge/discharge and long-term tests in Swagelok-type electrochemical cell (see Fig. 1).

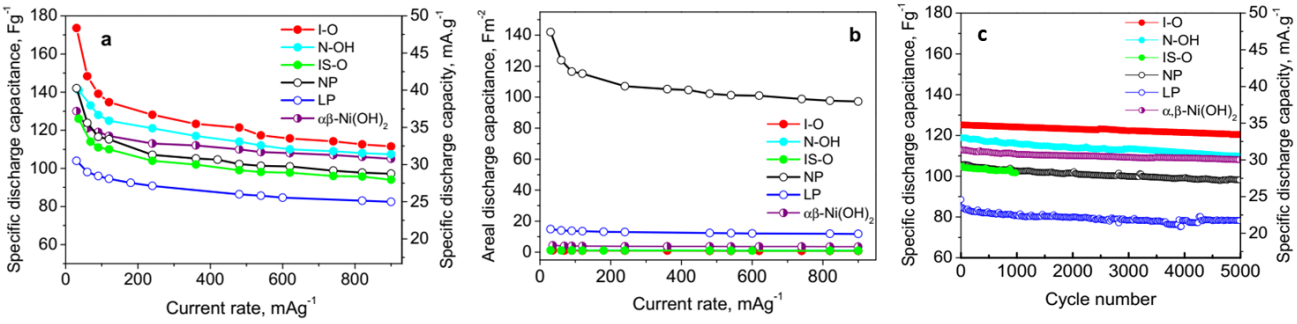

Figure 1. Specific discharge capacitance **(a)** and areal discharge capacitance **(b)** as a function of the current load of supercapacitor cells with different composite electrodes **(c)** Specific discharge capacitance (capacity) as a function of the cycle number at 240 mA/g of supercapacitor cells with different composite electrodes. For the sake of comparison, the discharge capacitance is also calculated in mAh/g.

The structure, morphology and porous texture properties of composites are analyzed by *post-mortem* powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and low-temperature nitrogen adsorption, respectively.

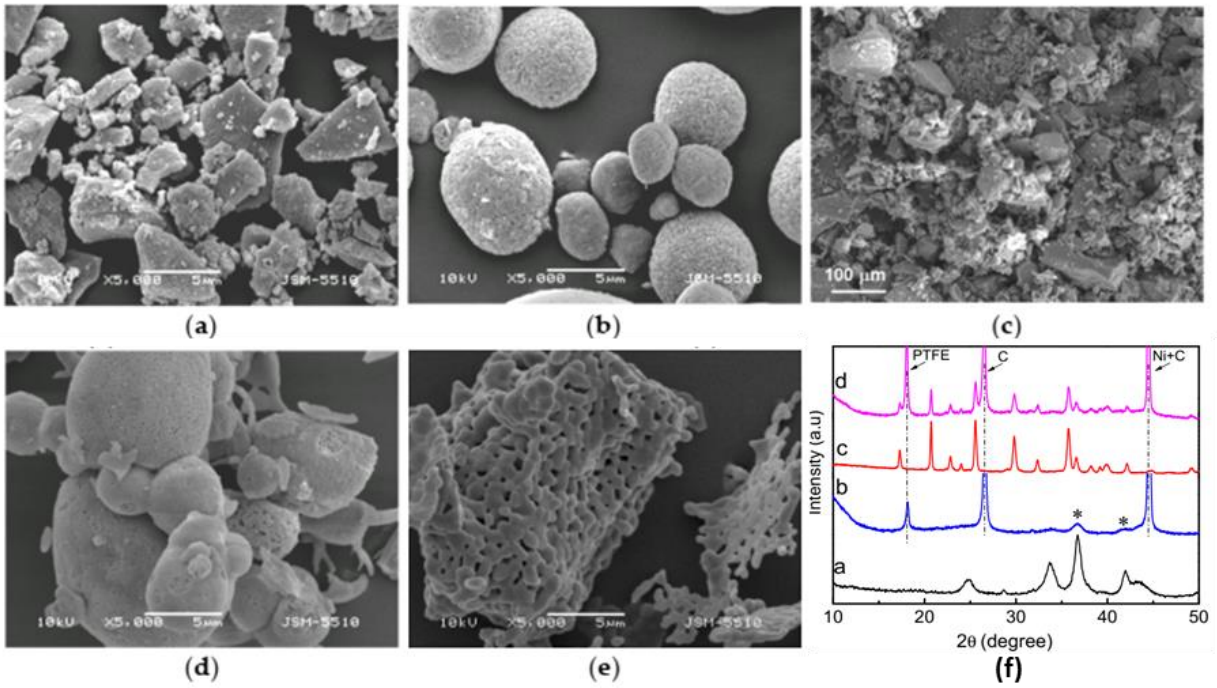

Figure 2. SEM images: **(a)** β-$Ni_{1/2}Mn_{1/2}(OH)_2$, **(b)** ilmenite $NiMnO_3$, **(c)** mixture of $NiMnO_3$ and $Ni_{1.5}Mn_{1.5}O_4$, **(d)** olivine $LiNi_{1/2}Mn_{1/2}PO_4$, **(e)** maricite $NaNi_{1/2}Mn_{1/2}PO_4$; **(f)** *Ex situ* XRD patterns of ilmenite (b) and phospho-olivine (d) electrodes after 5000 cycles. For the sake of comparison, the pristine ilmenite (a) and phospho-olivine (c) are also given. Symbols (*), (PTFE), (C) and (Ni) denote the peaks due to the ilmenite phase, PTFE, graphite and Ni foam, respectively.

The analytical results confirm that the investigated three types of crystal structures: oxides with ilmenite and spinel structures, hydroxides isostructural to β-$Ni(OH)_2$ and phosphates with olivine and maricite structures are able to simultaneously accommodate nickel and manganese ions [1]. The capacitance performances of oxides, hydroxides and phosphates depend mainly on whether the electrode contains simultaneously contains nickel and manganese in a ratio of one-to-one and, to a lesser extent, on the type of anionic constituents. Cycling stability becomes better when the morphology consists of spherical aggregates. Based on these findings, one can predict the electrode with the best capacitance performance.

References

1. L. Soserov, D. Marinova, V. Koleva, A. Stoyanova and R. Stoyanova, *Batteries* 8 (2022) 51.

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