

By use of TG-DTG diagrams studied by different authors it is shown that the pyrolysis of H_3PO_4 -activated carbonaceous material is delayed compared to the non- H_3PO_4 activated materials, wherein the shift of the main decomposition peak usually exceeds $300\text{ }^\circ\text{C}$ [8–9]. A progressive narrowing of the pores and loss of accessible surface area resulted from the secondary contraction exerts a dominant effect above $450\text{ }^\circ\text{C}$ [7]. Finally, in the range of $580\text{--}720\text{ }^\circ\text{C}$ the cleavage of previously formed bonds, and their subsequent recombination in the condensed poly-aromatic compounds has been proposed [8]. Nevertheless, recent studies in high temperature treatment of H_3PO_4 -impregnated graphene aerogels, attempted to bring a new look at the possibility of this method [10–11]. In particular, due to the evolution of elemental phosphorus occurring during activation when the temperature exceeds $800\text{ }^\circ\text{C}$, the additional nanoporosity can be formed.

In this study, a highly efficient method for high-temperature treatment of walnut shells in presence of mild $40\text{ wt.}\%$ H_3PO_4 is presented. The aim of work is to develop micro- and mesoporous ACs possessing developed specific surface area and a high volume of micropores. Furthermore, these ACs are used as electrode material in SCs to establish the influence of the processing temperature on the electrochemical charge storage.

2. Experimental

Cleaned, dried and crushed walnut shells (*Juglans regia*) were derived from local farms of Almaty province, Kazakhstan, and impregnated with $40\text{ wt.}\%$ aqueous solution of H_3PO_4 with ratio of activator to precursor equal to 3:1. Then resulting mixture was placed in a ceramic crucible and activated for 45 min at $400\text{ }^\circ\text{C}$, $500\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$ under nitrogen atmosphere inside a shaft furnace. Carbons obtained at these temperatures are described in manuscript as P-400, P-500 and P-800 respectively. The post-treatment of one sample (activated at $400\text{ }^\circ\text{C}$) was performed at $800\text{ }^\circ\text{C}$, further described in the text as P-400-M. The nitrogen adsorption isotherms were determined with an Autosorb-1 (Quantachrome instruments, UK) in the range of relative pressures from 0.005 to 0.991 realized at $-196\text{ }^\circ\text{C}$. BET specific surface area was calculated from the range of relative pressure values below 0.1. The modified model of non-local density functional theory (2D-NLDFT) was used to determine pore volume and pore size distribu-

tion (PSD). The morphology of ACs was investigated by scanning electron microscopy (SEM) using a QUANTA 3D 200i microscope («FEI», USA) with accelerating voltage of 15 kV and the elemental composition by using energy dispersive X-ray analyzer EDAX TEAM (Ametek, USA). Raman spectroscopy was performed with a Raman spectrometer Renishaw InVia Basis (Renishaw plc, UK) using excitation wavelength of 633 nm and exposure time 100 s.

For evaluating electrochemical performance of ACs in SCs, composite electrodes pellets by mixing $90\text{ wt.}\%$ of AC, $5\text{ wt.}\%$ of polytetrafluoroethylene (PTFE) from Sigma-Aldrich and $5\text{ wt.}\%$ of carbon black (C-65, Timcal C-ENERGY Imerys). Two-electrode cells were realized in Teflon Swagelok® vessel using 1 mol L^{-1} Li_2SO_4 aqueous electrolyte, Whatman GF/A membrane separator and SS 316L current collectors. The cyclic voltammetry (CV), galvanostatic charge/discharge (GCPL) and electrochemical impedance spectroscopy (EIS) in the range 1 mHz to 100 kHz were carried out by using a VMP-3 multichannel potentiostat/galvanostat (BioLogic Instruments, France).

3. Results and Discussion

SEM images in Fig. 1(a) present the surface morphology of ACs prepared through activation at temperatures from $400\text{ }^\circ\text{C}$ to $800\text{ }^\circ\text{C}$ resembling the loose cellular structure and possess highest open work texture represented by interconnected cavities formed owing to organic volatiles evolution. The release of volatiles resulted in reduced oxygen and the mineral part of carbonized material related with potassium leaching which was replaced by phosphorus. However, the mass content of phosphorus is reduced with increasing activation temperature from 500 to $800\text{ }^\circ\text{C}$. In such a case phosphate groups are formed that convert to polyphosphate groups [6–8], and apparently further decompose at higher temperatures; the similar trend was previously discussed in [12–13]. Consequently, the submicron sized channel openings and fissures protruding to the surface are formed which are clearly visible after post treatment in P-400-M.

The Raman spectra of resulting ACs in Fig. 1(b) display almost linear dependence between the intensity of D-band and the temperature of chemical activation. The gradual development of porosity, its reorganization and progressive narrowing of the nanopores might be associated with I_D/I_G ratio.