

ID No.: P16722

Form 7 / 様式 7

必ず ID 番号を記入すること

外国人特別研究員作成 / By Fellow

Be sure to enter the Fellow's ID number

2018 / 09 / 02
(YYYY) (MM) (DD)

JSPS Fellow's

Signature (Handwritten only):

Research Report (by Fellow)
(Cover Page)

I hereby submit the research report of my fellowship.

1. Name (Print) : Yusuf Valentino KANETI ✓
2. Nationality : Australia ✓
3. Host Institution : National Institute for Materials Science (NIMS) ✓
4. Host Researcher : Yusuke YAMAUCHI ✓
5. Title of Research in Japan : _____
MOF を出発原料として用いたキャパシタ用多孔質電極の合成 ✓
6. Fellowship Tenure : From 2016 / 09 / 03 To 2018 / 09 / 02 ✓
(YYYY) (MM) (DD) (YYYY) (MM) (DD)

Notes for writing the Research Report**Type this form except the date and the signature.**

Please prepare your Research Report in English or Japanese within three to ten pages including this page. The contents should include:

7. Background of Research

Traditional supercapacitors also known as electrochemical double-layer capacitors (EDLCs) typically employ carbon-based materials with high surface area and porosity. EDLCs store energy by forming an ionic double layer which diffuses very quickly, hence providing a very rapid discharge as well as higher power densities. However, the energy density of EDLCs and the charges which can be physically stored by EDLCs are quite low in aqueous as well as organic electrolytes. On the other hand, electrochemically active materials such as transition metal oxides (TMOs) and sulfides employ a reversible Faradaic reaction to store charges. TMOs have shown higher capacitance capabilities as well higher energy densities by at least an order of magnitude than those of carbon-based materials. However, the microstructure of the metal oxide materials may become distorted, and its original phase may be changed because of these continuous reactions, which ultimately results in poor cycling stability for commercial applications. Thus, the development of highly porous metal oxide nanostructures with excellent electrochemical properties is crucial for achieving high energy density and power density and PD in supercapacitors. The capacitance of TMO materials is strongly governed by several parameters including porosity (to enable a fast access for the electrolyte), crystallinity (to ensure the deep diffusion of the electrolyte), the size of the redox active species, as well as the surface area of the electrode materials (to enhance the contact area between the electrode materials and the electrolyte). To solve these problems, it is highly desirable to develop advanced electrode materials which exhibit high stability, high electrical conductivity, and permanent porosity with tunable pore size and pore volume for high-performance next-generation energy storage applications. It is expected that by combining metal oxide nanostructures with porous carbon materials to create porous oxide/carbon nanocomposites, electrode materials with enhanced energy and power densities may be obtained.

Lithium-ion batteries (LIBs) have long been considered as the most promising energy storage devices owing to their high energy density. However, the high cost and limited availability of lithium sources have prompted the search for suitable alternatives to LIBs. Sodium-ion batteries (SIBs) have recently been proposed as possible alternatives to LIBs, due to their abundance, low cost and environmental friendliness.

However, SIBs usually suffer from low reversible capacity and poor cycling stability at high current rates owing to the larger ionic radius of Na^+ (1.02 Å) compared to that of Li^+ (0.76 Å), which lead to large volume expansion and irreversible phase transition during sodiation/desodiation. While TMOs may exhibit high specific capacities when used as anode materials for SIBs, they tend to undergo large volume changes during sodiation/desodiation. Hence, the addition of a carbon matrix via hybridization is necessary to improve the cycling and rate performance of TMO-based anodes for SIBs. Potassium-ion batteries (KIBs) have also been considered as a potential alternative to LIBs for grid-scale electrochemical energy storage due to their abundant reserves and similar working principles. However, similar to Na^+ , the larger radius of K^+ compared to Li^+ is a major obstacle for the large-scale utilization of KIBs. Therefore, finding suitable host materials for potassium ions is of utmost importance in KIBs.

Metal-Organic Frameworks (MOFs) are defined as compounds consisting of metal ion nodes and organic linkers. In recent years, MOFs have attracted considerable interests as versatile precursors for the derivation of various porous nanomaterials, including carbons, metal oxides, metal sulfides, metal phosphides, metal carbides due to their high surface area (up to $10,000 \text{ m}^2 \text{ g}^{-1}$) and highly controllable composition, structures, and porosity. Furthermore, MOFs can be conveniently converted into porous metal oxides, carbons or oxide/carbon composites depending on their calcination conditions while retaining their inherent properties, further highlighting their advantages. However, as the diverse structure, composition and porosity of MOFs can directly affect their electrochemical performance for energy storage systems (e.g., supercapacitors, lithium-ion batteries, sodium-ion batteries, potassium-ion batteries), the specific impacts of these parameters on the electrochemical performance of porous MOF-derived nanostructure /nanocomposites need to be further investigated to ensure their successful application in energy storage systems. Therefore, in this project, we aim to control the morphology, composition, and porosity of the MOF-derived porous nanomaterials/composites to optimize their electrochemical performance for various energy storage devices,

8. Research methodology

➤ Sample characterization

The purity and phase composition of the MOF precursors and MOF-derived porous materials were analyzed by X-ray diffraction pattern (XRD) using a Rigaku RINT 2500X diffractometer with a monochromated $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ Å}$). The morphological observations of these samples were performed using field-emission scanning electron microscope (FESEM, Hitachi SU-8000) operated at 5 kV and transmission electron microscope (TEM, JEM-2100F) operated at 200 kV. The thermal decomposition behaviours of the MOF precursors were analyzed by thermogravimetric analysis (TGA) using a Hitachi HT-Seiko Instrument Exter 6300 TG/DTA from room temperature to 1000°C under air atmosphere with a fixed heating rate of $10^\circ\text{C}/\text{min}$. Surface composition and electronic states of the samples were analyzed using X-ray photoelectron spectroscopy (XPS) on a PHI Quantera SXM (ULVAC-PHI). All XPS spectra were calibrated to the C 1s peak at 285.0 eV. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was conducted using a Hitachi SPS3520UV-DD to analyze the metal content in the MOF precursors and the final MOF-derived porous materials. Nitrogen (N_2) adsorption-desorption measurements were conducted using a Belsorp-mini II Sorption System at 77 K. The specific surface areas and pore volumes of the samples were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. Prior to the BET measurements, the samples were degassed under vacuum at 150°C for 16 h.

➤ Electrochemical measurements

Supercapacitor tests

The electrochemical measurements for supercapacitors were carried out with an electrochemical workstation (CHI 660E, CH Instruments, USA) using standard three-electrode and two-electrode system measurements. For the three-electrode system, Ag/AgCl was used as the reference electrode and a platinum wire was used as a counter electrode and all the measurements were carried out in an aqueous 3.0 M KOH electrolyte. The working electrodes were prepared by mixing the active electrode material (80%) with poly(vinylidene difluoride) (PVDF) (20%) in N-methylpyrrolidinone (NMP) solvent. The resultant slurry was then coated onto graphite substrates and dried at 60°C for 12 h. Each electrode contained 1 mg cm^{-2} of the active material. The specific capacitance value of each electrode was calculated using cyclic voltammetry (CV) using the following equation:

$$C = \frac{1}{ms(V_f - V_i)} \int_{V_i}^{V_f} I(V) dV$$

where C is the specific capacitance, s is potential scan rate, V is the potential window, the integration of $I(V) dV$ is the discharging part of the cyclic voltammograms, m is the mass of the active material. For the two electrode-system, a membrane consisting of Whatman glass microfiber filter was used as the separator with the electrolyte. The specific capacitance was calculated by utilizing the following equation:

$$C = \frac{I \times \int V dt}{M \times \Delta V^2}$$

where C is the gravimetric capacitance, V is a potential window, I is the current, t is the discharge time, and M is the total mass of active materials of both electrodes.

The electrochemical properties of the assembled asymmetric supercapacitor (ASC) cell were investigated by using CV and galvanostatic charge-discharge (CD) measurements. For the CD measurements of the two-electrode ASC cell, a positive electrode consisting of the MOF-derived materials and a negative electrode consisting of graphene oxide (GO) with a similar charge capacity were employed. To achieve a stable ASC cell operated over a wide potential window, it is important to achieve a mass balance between the positive and negative electrodes, according to the equation:

$$\frac{m_+}{m_-} = \frac{C_- V_-}{C_+ V_+}$$

where C_+ and C_- are the specific capacitances, V_+ and V_- are the potential windows, and m_+ and m_- are the mass of the positive and negative electrode materials, respectively, which were obtained in a three-electrode system. In the case of symmetric (or linear) galvanostatic discharge curve (GDC) behavior, the charge/voltage ratio remains constant over the entire voltage window, and the energy density E can be calculated by applying the following equation:

$$E = \frac{CV^2}{2}$$

However, as our GDC is non-symmetric and hence, the Faradaic reaction charge/voltage ratio does not remain constant, but rather varies with time. As such, the energy density (E) and power density (P) of the assembled ASC were calculated using the equations:

$$E = i \int V dt$$

$$P = \frac{3600 \times E}{t}$$

where i is the current density, $\int V dt$ is the galvanostatic discharge current area and t is the discharge time.

Sodium-ion batteries

The electrochemical properties of the samples were evaluated using standard CR2032 coin-type cells. The working electrodes were prepared by mixing the active material, acetylene black (super P), and poly(vinylidene fluoride) (PVDF) in a weight ratio of 70: 15: 15 in N-methyl pyrrolidinone (NMP) and the resulting slurry was coated uniformly on pure Cu foil and dried at 120 °C under vacuum for 12 h. Pure sodium foil was used as the counter electrode, glass fiber as the separator, and a solution of 1.0 M sodium NaClO₄ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1: 1 by volume) as the electrolyte. The battery assembly was carried out in an argon-filled glove box with concentrations of moisture and oxygen below 1 ppm. Galvanostatic charge-discharge tests were carried out using a Land CT 2001A battery test system at different current densities in the voltage range of 0.01–3.0 V. The Coulombic efficiency of the anode during charge is given by the equation:

$$\text{Coulombic efficiency} = Q_{\text{charge}}/Q_{\text{discharge}} \times 100\%$$

Potassium-ion batteries

The coin cell (CR 2032) was used as a testing battery. To prepare the working electrode, the as-obtained materials (80 %), Ketjen Black (10 %), and PVDF (10 %) were mixed in NMP. The slurry was coated onto a copper current collector and dried at 100 °C overnight in a vacuum oven. The typical mass loading of electrode was about 2 mg/cm². Glass fibers (GF/D) from Whatman® were utilized as a separator. Potassium metal was utilized as counter/reference electrodes. The electrolyte used was prepared by dissolving 0.8 M KPF₆ in a solvent mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in volume). All coin cells were assembled in an argon-filled glove box with moisture and oxygen levels below 0.1 ppm. The galvanostatic charge/discharge profiles were investigated by a Land CT 2001A battery test system (Wuhan, China). The cyclic voltammetry (CV) curves were measured on a CHI electrochemical workstation (CHI, 660 E). The mass of the active material was calculated based on the mass of the sample without counting Co (about 15% in electrode).

9. Results/impacts

➤ Significant research findings

- *Angew. Chem. Int. Ed.*, 2017, 56, 8435-8440: This work reported the novel derivation of *porous three-dimensional (3D) graphitic carbon networks* (**Figure 1a**) from the downsizing of the MOF, zeolitic imidazolate framework-67 (ZIF-67) particles which exhibited a high specific capacity of 100 mAh g⁻¹ at a high current density of 2000 mA g⁻¹ when employed as an anode material for potassium-ion batteries (KIBs) (**Figure 1b**). Furthermore, the fabricated 3D carbon networks could maintain 75% of the initial capacity after cycling for 500 cycles at a current density of 50 mA g⁻¹ (**Figure 1c**). Furthermore, in this work, the first *calculation procedures to predict the formation tendency of such graphitic networks* based on the size of the ZIF-67 particles were established.

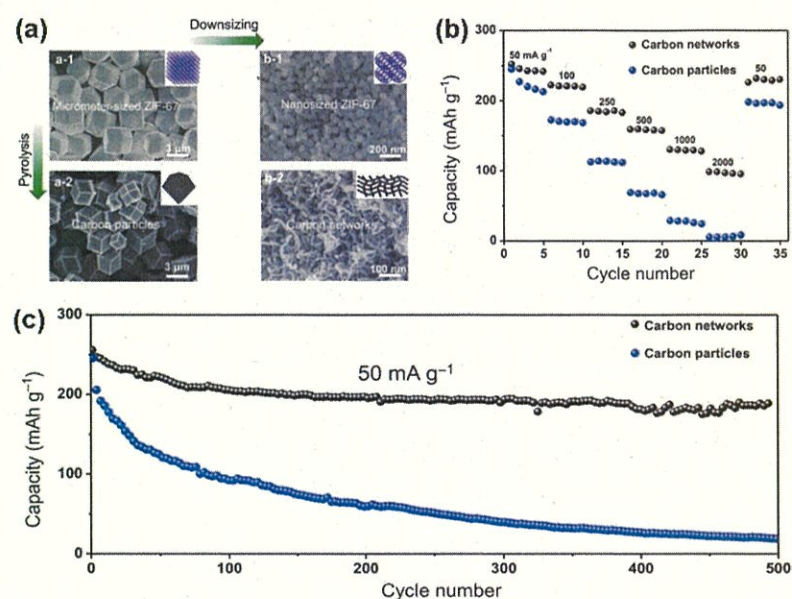
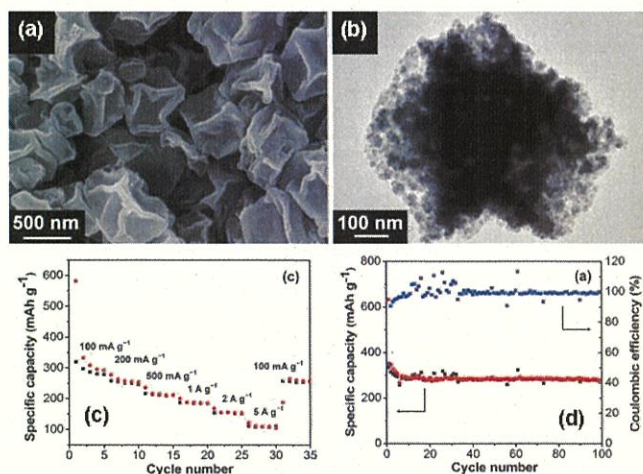


Figure 1. (a) SEM images of the micrometer-sized ZIF-67 particles (a-1) and nanosized ZIF-67 particles (b-1). SEM images of the carbon particles (a-2) and carbon networks (b-2) obtained by the pyrolysis of the ZIF-67 particles shown in (a-1) and (b-1), respectively. Comparison of (b) the rate performance and (c) cycling performance of the 3D carbon networks and carbon particles for potassium-ion batteries (KIBs)

- *J. Mater. Chem. A*, 2017, 5, 15356-15366: The first report on the derivation of *porous ternary Ni-doped Co/CoO/carbon nanocomposites from bimetallic Ni-Co MOFs* (**Figure 2a-b**) as excellent anode materials for sodium-ion batteries with high sodium-storage performance (a high discharge capacity of 218 mA h g^{-1} at a high current density of 500 mA g^{-1}) (**Figure 2c**) and good cycling stability with a high discharge capacitance retention of 87.5% after 100 cycles at a high current density of 500 mA g^{-1} (**Figure 2d**).



- *Chem. Mater.*, 2018, 30, 4401-4408: Hollow ZnO/C composite polyhedrons (**Figure 3a-e**) were synthesized via a newly proposed one-step method through the hydrothermal reaction of ZIF-8 polyhedrons with glucose at 180°C followed by annealing at 500°C for 3 h under nitrogen atmosphere. When employed as an electrode material for supercapacitor, the hollow ZnO/C composite showed a high specific capacitance of 394 F g^{-1} at a high current density of 1 A g^{-1} , which is higher than many previously reported capacitance values obtained for ZnO/carbon composites. When the current density is further increased by 60 times to 60 A g^{-1} , the capacitance of the hollow ZnO/C composite still maintained an impressive specific capacitance of 225 F g^{-1} , corresponding to a relatively high capacitance retention of 57% (**Figure 3f-g**).

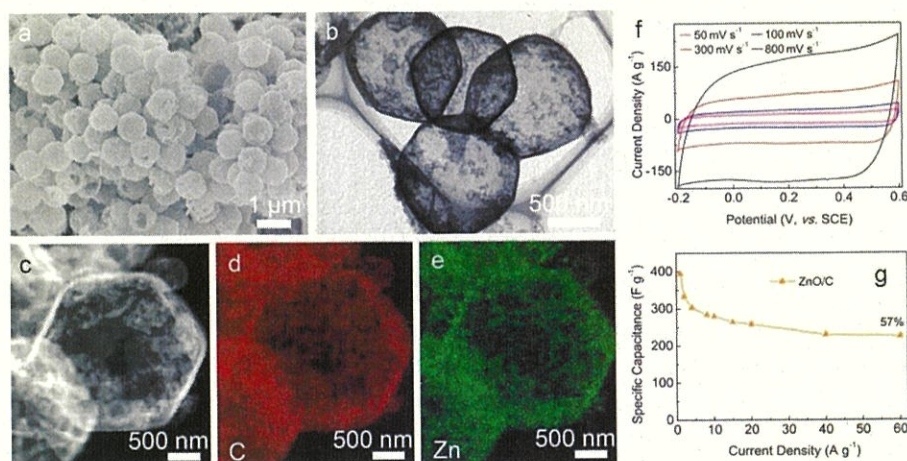


Figure 3. (a) SEM image, (b) TEM image, (c) STEM image, and (d-e) elemental mapping of the hollow ZnO/C polyhedrons obtained from the hydrothermal reaction between ZIF-8 particles and glucose at 180 °C followed by annealing at 500 °C for 3 h under nitrogen atmosphere.

- *ACS Appl. Energy Mater.*, 2018, 1, 2007-2015: This work reports the first synthesis of graphitic carbon/Ni-Co/Co_{0.75}Ni_{0.25} ternary composites (NC-800, **Figure 4a**) via direct carbonization of bimetallic NiCo-MOF-74 particles at 800 °C under N₂ atmosphere as well as the first synthesis of binary NiCoO₂/Ni-Co (NC-350, **Figure 4b**) composites via the heat treatment of NiCo-MOF-74 in air at 350 °C. When evaluated as electrode materials for supercapacitors, the graphitic carbon/Ni-Co/Co_{0.75}Ni_{0.25} and NiCoO₂/Ni-Co composite electrodes exhibited high specific capacitances of 715 F g⁻¹ and 513 F g⁻¹, respectively, at a high current density of 1 A g⁻¹ (**Figure 4c**). Furthermore, these hybrid materials also displayed good cycling stability with no visible degradation in their specific capacitance after 2500 cycles.

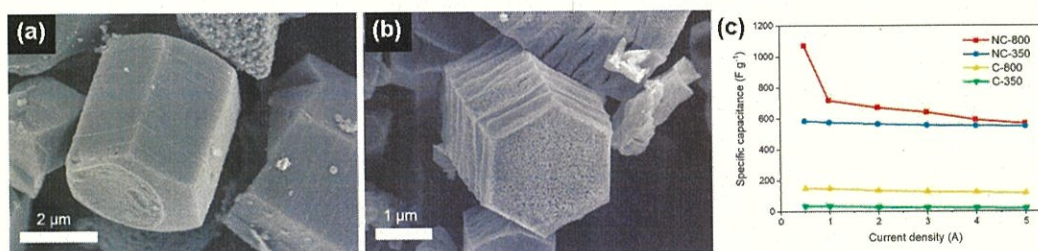


Figure 4. SEM images of (a) graphitic carbon/Ni-Co/Co_{0.75}Ni_{0.25} (NC-800) and (b) NiCoO₂/Ni-Co (NC-350) composites derived from Ni-Co-MOF-74 and (c) the corresponding specific capacitance versus current density plots (from 0.5 to 5 A g⁻¹) for NC-800 and NC-350.

- *Chem. Comm.*, 2018, 54, 8514-8517: This work reports one of the most effective catalysts for carbon monoxide oxidation based on gold-loaded mesoporous maghemite (γ-Fe₂O₃) nanoflakes which exhibit nearly 100% CO conversion and a very high specific activity of 8.41 mol_{CO} g_{Au}⁻¹ h⁻¹ at room temperature.

➤ Research outcomes

- During the JSPS Fellowship, I have published a total of **28** journal articles, including **10 first-authored articles** and **18 co-authored articles**.
- From a total of 28 journal articles, **13 papers** were published in leading Materials Science and Chemistry journals with **impact factor (IF) > 8.0** and **15 papers** in high quality journals with **IF > 5.0** (e.g., *Advanced Materials*, *ACS Nano*, *Angewandte Chemie International Edition*, *Nano Energy*, *Account of Chemical Research*, *Materials Horizons*, *Chemistry of Materials*, *Journal of Materials Chemistry*, *Small* and *ACS Applied Materials and Interfaces*).
- As of 2018/08/26, **3** of these papers have been listed as “**Highly Cited Papers**”, a designation that reflects papers of exceptional impact that are in the **top 1% of Materials Science, Chemistry and Physics field**, including one “**Hot Paper**” in the **top 0.1% of papers in the academic field of Chemistry and Materials Science** based on citations in the past two years (Essential Science Indicators from Web of Science as of 2018/08/26).

- My research work with NBC Mesh Tech. (Japan) on the development of room-temperature carbon monoxide (CO) oxidation catalyst using 2D mesoporous iron oxide nanoflakes has been highlighted by Nikkei (<https://www.nikkei.com/article/DGXMZO33738950S8A800C1L60000/>) and NIMS press release (<http://www.nims.go.jp/news/press/2018/07/201807190.html>) and a patent application is currently being prepared by NBC Mesh Tech based on this research work.

10. Research Presentations during the period of the fellowship (Name of the conference, title, place, date)

- No conference presentation
- 11. A list of paper published during or after the period of the fellowship, and the names of the journals in which they appeared (Please fill in the format below). Attach a copy of each article if available.**

- Please see attachment

12. Awards during the period of the fellowship (Name of the award, Institution, date etc.)

- 2nd Prize MANA Nano Art Research Image Competition (National Institute for Materials Science, 2018/05/31)

--