Fabrication and electrochemical performance of lithium polymer battery using mesoporous silica/polymer hybrid electrolyte

Masanobu NAKAYAMA, Takashi OKAJIMA, Yoshihiro YAMAMOTO, Shinji BABA, Kaede IIZUKA, Masayuki NOGAMI, Dai MOCHIZUKI, Takanori KIGUCHI and Shigeki KUROKI

1) Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso, Showa, Nagoya 466–8555, Japan
2) Japan Science and Technology Agency, PRESTO, 4–1–8 Honcho Kawaguchi, Saitama 332–0012, Japan
3) Unit of Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Katsura, Sakyoku, Kyoto 615–8520, Japan
4) R&D division, World Interc Co., Ltd., 4F No.2 Quest Bldg.1–3–9 Bashaku Kokurakita-ku, Kitakyushu 802–0077, Japan
5) Department of Applied Chemistry, Tokyo Institute of Technology, 2–12–1 Ookayama, Meguro-ku, Tokyo 152–8552, Japan
6) Institute for Materials Research, Tohoku University, 2–1 Katahira, Aoba-ku, Sendai 980–8577, Japan
7) Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2–12–1 Ookayama, Meguro-ku, Tokyo 152–8552, Japan

Development of all solid-state Li secondary based on the use of dry polymer or inorganic electrolytes is vital as they will be free of solvent leakages and improve inflammability. However, both are still under development for many years due to low ionic conductivity, poor mechanical property and/or large internal impedance associated to poorly defined interfaces. In this paper, we report on a preparation and physicochemical property of mesoporous silica (MPS)/Li conductive polyethylene oxide (Li-PEO)-based polymer hybrid electrolytes (MPS+Li-PEO), and electrochemical performance of the Li/MPS+Li-PEO/LiFePO4 cell. The hybrid electrolytes showed an improvement of Li+ transportation number and a decrease of melting point and glass transition temperature, indicating a positive hybrid effect, or deviation from rule-of-mixtures behavior. The Li/MPS+Li-PEO/LiFePO4 cell showed a stable charge-discharge capacity of >70 mAh g⁻¹ for 100 cycles at moderate temperature of 60°C and rate of 0.2 C, whereas severe capacity fade began after several of cycles for the cell using conventional Li-PEO electrolyte. AC impedance measurements revealed that the interface Li exchange between electrode and electrolytes related to the stable cyclic performance for the cell using hybrid electrolytes.

Key-words : Lithium polymer batteries, Hybrid electrolytes, Mesoporous silica, Interfacial impedance

1. Introduction

Large-scale lithium secondary batteries have attracted interest for electric vehicles and the storage of renewable energy in order to address energy and environmental issues. However, safety problems arising from the flammability of organic solvents prevent the realization of large-scale batteries. Thus, all-solid-state lithium polymer batteries (LPBs) are attractive because they are safe and easily formable.

We have previously reported an LPB with a polyethylene (PEO)-based solid polymer electrolyte (SPE) which showed a reversible capacity of more than 100 mAh g⁻¹ over 150 cycles at a rate of 0.2 C and a moderate temperature of 30°C. (Note that the unit C refers to the C-rate, where 1 C rate represents a one-hour complete charge or discharge.) Thus, the rate of 0.2 C corresponds to 5 h for full charge or discharge. Gradual capacity fade occurred after ~200 cycles. The fading was accelerated by increasing the temperature to 60°C, and severe degradation occurred within 100 cycles. Hence, an improvement in the electrochemical durability is required to produce a commercial, large-scale LPB. The capacity degradation was investigated by using ex situ and in situ techniques, such as electrochemical impedance spectroscopy (EIS), thickness monitoring of the LPB cell, and NMR-imaging techniques. The degradation was attributed to the poor mechanical properties of the SPE, which reduced the electrolyte/electrode contact. This causes an increase of local polarization, resulting in the side reaction of Li salt decomposition at the electrode/electrolyte interface. In fact, the acceleration of the capacity fading at elevated temperature at 60°C may relate to the weakening of the mechanical property of PEO based SPE, since the operating temperature is close to the melting temperature of PEO matrix.

Ceramic/Li+ conductive PEO (Li-PEO) hybrid electrolytes contain ceramic particles that improve their mechanical strength. For example, Croce et al. reported notable charge-discharge cycle performance with a capacity retention of 100 mAh g⁻¹ at 105°C and at the rate of 1.0 C for a Li/LiFePO4 cell using Al2O3 particle/Li-PEO hybrids. Sun and Takeda et al. also showed improved ionic conductivity by addition of BaTiO3 into PEO based SPE and stable electrochemical cycles by the use of the their developed SPE. Thus, the ceramics addition into PEO based
SPE are attractive technique for developing all solid-state LPBs.\(^{12,13}\)

In this study, we used mesoporous silica (MPS)/Li\(^+\) conductive PEO (Li-PEO) hybrid electrolytes in lithium polymer batteries to improve the mechanical strength of the SPE. MPS is composed of stacked SiO\(_2\) channels arranged in a hexagonal array with pore sizes ranging from 2 to 10 nm. It has been reported that the insertion of Li-PEO into the mesopores of MPS results in increases in the ionic conductivity, in the Li\(^+\) transference number, and in the mechanical strength. Moreover, the temperatures of the glass transition and the melting point of the crystalline phase are increased by the introduction of MPS, which enhances the Li\(^+\) migration and the segmental motion of the polymer chain.\(^{14,15}\) We fabricated SPEs using MPS/Li-PEO hybrids for all-solid-state LPBs and studied their electrochemical properties.

2. Experimental

MPS was synthesized by the sol–gel method based on the references.\(^{16}\) Brij 56 (Aldrich) and ethanol were stirred at 60°C for 10 min, and then tetraethyl orthosilicate (TEOS; Tokyo Chemical Industry) and HCl aq. (35%, Kishida Chemical) were added. The solution was dried for 24 h and heated at 500°C for 5 h. The molar ratio of TEOS/Brij 56/H\(_2\)O/ EtOH/HCl was 1.0:0.25:8.0:200:0.001. The MPS/Li-PEO hybrid polymer electrolyte was prepared with MPS, PEO with a linear architecture (MW: 10\(^6\), Aldrich), and lithium bis-trifluoromethanesulfonimide [LiN(CF\(_3\)SO\(_2\))]\(_2\) (LiTFSI, Fluka). A mixture of PEO/LiTFSI (molar ratio 20:1) was dissolved in acetonitrile (MeCN) and stirred for 24 h at room temperature. Various amounts of MPS particles were dispersed in the solution. The mixture of Li-PEO and MPS was dried for 5 h under ambient conditions, and then vacuum dried at 120°C for 24 h in a Teflon vessel. The thickness of the MPS/Li-PEO electrolytes ranged from 0.5 to 0.7 mm. Samples of the MPS and MPS/Li-PEO hybrids were characterized by X-ray diffractometry (XRD), BET measurements, high-resolution transmission electron microscopy (TEM), and differential scanning calorimetry (DSC). The diffusion properties of the ions were evaluated by AC impedance and pulse field-gradient stimulation echo (PGSTE)-NMR measurements for \(^1\)H, \(^7\)Li, and \(^19\)F nuclei. LiFePO\(_4\) with an olivine structure (Aldrich) was used as the electrode active material. The electrode sheets consisted of the active material (80 wt%), acetylene black (5 wt%) as the electrically conductive agent, and Li-PEO (15 wt%) as the lithium ion conductor and binder. The Li-PEO phase was dissolved in MeCN and the resulting slurry containing active material and acetylene black was cast onto aluminum sheets. The MeCN was removed by evaporation in a vacuum oven and the sheets were then pressed. The cathode sheets, except for the Al sheet, were 30–50 \(\mu\)m thick. The cathode sheet, the SPE film, and the lithium foil were cut into disks, which were stacked inside a coin-type cell. The details of the preparation of the cathode sheets have been reported elsewhere.\(^{7,9,10}\)

Charge/discharge tests of the LPBs were performed galvanostatically at cut-off voltages of 3.0–3.8 V versus Li\(^+\)/Li at an operation temperature of 60°C. Before the electrochemical measurements, the coin-type cells were aged in a temperature-controlled chamber at the cell operation temperature for 24 h to enhance adhesion at the Li/SPE and the SPE/LiFePO\(_4\) interfaces. The AC impedance measurements for the LPBs were performed using a multichannel potentiostat equipped with impedance modules (VMP3, Bio-logic). The frequency range was \(10^{-2}\) to \(10^5\) Hz.

3. Results and discussion

Figures 1(a)–1(c) respectively show a TEM image, an XRD pattern, and the BET pore distribution diagram for a prepared MPS sample. The TEM image confirmed the formation of one-dimensionally ordered mesopores with a periodicity of \(\sim 34\) Å in the SiO\(_2\) matrix, and the XRD pattern showed that the periodicity of the mesopores was \(\sim 40\) Å. Therefore the two methods produced similar results. The BET measurements showed that the pore diameter of the MPS sample was \(\sim 34\) Å, showing good accordence with TEM images, and thus the difference between the periodicity and the pore diameter was the thickness of the SiO\(_2\) wall of the mesoporous structure (\(\sim 6\) Å). The MPS/Li-PEO hybrids did not appear to contain mesopores. [Fig. 1(c)] This suggests filling of the Li-PEO electrolytes into the mesopores, or encapsuration of both end of the one-dimensional pore. The DSC profiles of the MPS/Li-PEO hybrids with various weight ratios are shown in Fig. 2. The endothermic peaks during heating and the exothermic peaks during cooling between 30 and 60°C showed hysteresis, ascribed to the melting and the partial

Fig. 1. (a) HR-TEM images, (b) powder XRD patterns, and (c) pore size distributions from desorption branches of N\(_2\) adsorption/desorption isotherms for the synthesized MPS. The closed and open circles correspond to before and after Li-PEO insertion, respectively.
formation of the crystalline phase, respectively. A change in heat capacity caused by the glass transition was observed from \(1^\circ\text{C} \) to \(40^\circ\text{C} \).

Figure 2(c) summarizes the melting temperature \( (T_m) \) and the corresponding endothermic peak area per unit weight of the Li-PEO component. Both the \( T_m \) and the peak area were reduced by the addition of MPS to Li-PEO, which is consistent with previous studies. In particular, Li-PEO with 60 wt% MPS did not show a melting/crystallization peak. Therefore, MPS suppressed the crystallization of the Li-PEO phase. Because the crystalline phase does not contribute to the Li\(^+\) migration, the suppression of crystallization may improve the Li\(^+\) conductivity. The glass transition temperature \( (T_g) \) also decreased as the amount of MPS was increased. Generally, \( T_g \) is related to the segmental motion of the polymer chains which is the driving force of ion transport in polymers. Therefore, the addition of MPS to Li-PEO increased the mobility of the polymer chains. The shift in \( T_m \) and \( T_g \) is also evidence of a positive hybrid effect, or deviation from rule-of-mixtures behavior.

An AC impedance technique was used to construct the Arrhenius plot of the temperature dependence of the ionic conductivity [Fig. 3(a)]. For the Li-PEO electrolyte, the peak was around 55°C, which was attributed to the melting of crystalline phase during heating. The ionic conductivity decreased monotonically with the addition of MPS, although the DSC measurements indicated a positive hybrid effect for the segmental motion in the PEO phase. This may stem from a decrease in the volumetric fraction of the PEO conductive phase, and an increase in the MPS inert phase. The effect of the enhanced segmental motion was relatively small compared with the decrease in the volumetric fraction of the conductive phase.

The AC impedance technique cannot distinguish the species of conductive ions. Thus, the estimated conductivity included the proton, anion (TFSI\(^-\)), and lithium ion contributions. Proton conductivity was considered a possibility, owing to the surface acidity of the MPS silanol group. To clarify the contribution of proton conduction, the ion exchange reaction was conducted by soaking the MPS in aqueous 1 M LiOH or 1 M LiCl for 24 h at ambient temperatures. For the electrolytes containing 10 wt% MPS, the ionic conductivity for hybrid MPS electrolytes subjected to the ion exchange reaction agreed well with that for electrolytes not subjected to the reaction [Fig. 3(b)]. Therefore, the proton conductivity was probably negligible.

Table I contains the transport number of Li\(^+\) estimated by PGStE-NMR and by the DC polarization method reported by Evance et al. In PGStE-NMR, the diffusion attenuation of the spin–echo, from which the diffusion coefficients of the Li and F nuclei, \( D_{Li} \) and \( D_{F} \), were estimated at 60°C, is given by Eq. (1):

\[
A(g) = A(0) \exp(-\gamma^2 B^2 g^2 D(\Delta - \sigma/3)).
\]  

The details of Eq. (1) are described elsewhere. According to Tabata et al., the transport number, \( t_{Li} \), can be defined by
Eq. (2), which assumes a small interaction between the cation and the anion, and almost unity for the dissociation ratio:

\[ t_{\text{Li}} = \frac{D_{\text{Li}}}{D_{\text{Li}} + D_{\text{F}}} \]  

(2)

The DC polarization method used Eq. (3) for the Li/SPE/Cu cell at 60°C for 48 h, with a DC polarization of 0.2 V:

\[ t_+ = \frac{I_{(0)} R_{(0)} (\Delta V - I_{(0)} R_{(0)})}{I_{(0)} R_{(0)} (\Delta V - I_{(\infty)} R_{(\infty)})} \]  

(3)

where \( I \) is the direct current, \( \Delta V \) is the applied direct voltage, and \( R_0 \) and \( R_t \) correspond to the bulk and interfacial (Li/SPE) resistance for the SPE. The subscripts 0 and \( \infty \) refer to the initial and steady states, respectively. The DC polarization method showed a slightly higher transport number for Li than the PGStE-NMR method. The DC polarization method usually overestimates the transport number of Li, because of the technical difficulty in measuring the current of the DC voltage pulse at 0 s. Therefore, this degree of consistency may be adequate to show that an increase in the amount of MPS led to an increase in the transport number of Li.

The bulk properties of SPEs show that the addition of MPS to the SPE film exerted several favorable effects on the LPBs: lowering the melting and glass transition temperatures, increasing the transport number of \( \text{Li}^+ \), and improving the mechanical properties of the SPE, which is consistent with previously published studies.\(^{14,15}\) However, the total ionic conductivity was reduced as the amount of MPS increased at less than 60°C, because of the decrease in the fraction of the conductive PEO phase. (The ionic conductivity is improved slightly at more than 60°C for SPE with a weight ratio of Li-PEO/MPS of 9:1.) Therefore, the SPE film with a weight ratio of Li-PEO/MPS of 9:1 was used in the LPBs, unless otherwise stated.

**Figure 4** shows the charge-discharge profiles of the Li/LiFePO\(_4\) cell which contained the SPE film with MPS (LPB-MPS) and without MPS (LPB-noMPS), for selected cycle numbers. The reaction voltages were observed around 3.4 V between charging and discharging, which agrees with previous results for the two-phase coexistence reaction in an olivine LiFePO\(_4\) cathode.\(^{7,8}\) The corresponding capacity retention, Coulombic efficiency, and quasi-polarization with cycle numbers are shown in **Figures 5(a)–5(c),** respectively. The quasi-polarization is defined as half the difference in the averaged voltage between the charge and discharge reaction, which can be used to estimate roughly...
the change in the polarization during cycling. The LPB-noMPS showed a larger capacity (~100 mA h g⁻¹) during the initial ~10 cycles, followed by a sharp decrease in capacity. This trend in degradation was observed for the other LPBs with the same Li/SPE/LiFePO₄ configuration, and has been reported previously.²⁴ However, the cells which contained LPB-MPS showed stable capacity retention for 100 cycles, although the capacity of the cell (70–90 mA h g⁻¹) was smaller than that of the initial cycles for LPB-noMPS. The Coulombic efficiencies for LPB-noMPS and LPB-MPS were almost unity (100%) except for first cycle. Thus, the capacity fade observed in the LPB-noMPS was not caused by a continuous irreversible side reaction after second cycle between the charge and discharge. In LPB-noMPS, the quasi-polarization curve showed a gradual increase with the capacity fade after ~10 cycles, whereas there was no marked change in the quasi-polarization for LPB-MPS during 100 cycles. Therefore, the capacity fade in LPB-noMPS can be attributed to the increase in the internal resistance of the cell except for the SEI formation at the first cycle. The quasi-polarization was further characterized by measuring the evolution of the electrochemical AC impedance spectra during the cycles. Figure 6(a) shows the typical impedance spectra of LPB. The spectra consisted of two curves in the higher frequency region (regions 2 and 3), and a straight line at around 45° against the real part of the impedance axis at lower frequencies (region 4). According to previously published results,²⁴,³⁵ the two curves in the higher and lower frequency regions (regions 2 and 3) correspond to a charge-transfer reaction at the Li metal/SPE interface and the SPE/LiFePO₄ interface, respectively. This interpretation is supported by the fact that the frequency (~2000 Hz) for the curve of the symmetrical Li/SPE/Li cell agrees with that for the Li/SPE charge transfer curve in Fig. 6(a). The intersection of the spectra at the highest frequency with the Z' axis corresponded to the bulk resistance of the SPE film [arrow 1, Fig. 6(a)]. The straight line at lower frequencies was attributed to the diffusion driven concentration gradient around the SPE/LiFePO₄ interface (region 4). Based on this interpretation, the impedance spectra was fitted using the equivalent circuit shown in Fig. 6(b), which was modified from the circuit previously proposed in the literature.²⁵ In the figure, R₁, R₂, and R₃ represent the resistance caused by the ionic conduction in bulk SPE, the charge transfer at the Li-metal/SPE interface, and the charge transfer at the SPE/cathode interface, respectively. CPE₁ and CPE₂ are the constant phase elements, denoted by Z''_CPE = A/(jω)^(-α), which were used in place of the capacitance, and incorporated the distribution of the relaxation time or the non-uniform distribution of current caused by the roughness of the electrode. The lowest frequency region was fitted by adding the infinite length Warburg (ILW) impedance, Z''_ILW = Z₀/(jω)^0.5. The details of the impedance components used in our equivalent circuit model are described by Bard and Faulkner.²⁶ Typical curve-fittings are shown in Fig. 6(a); good agreement between the experimental and the calculated impedance spectra was observed. The goodness of fit, χ², was less than 5 × 10⁻⁴ for all the fitting procedures. The best fitted resistances, R₁, R₂, and R₃, are summarized in Fig. 7 as a function of the cycle number for LPB-noMPS and LPB-MPS. For both LPBs, the internal resistance, R₁ and R₃, was almost unchanged with the number of cycles. However, a continuous increase in R₂ was seen in LPB-noMPS during the capacity fade. Therefore, the degradation of the LPB was related to a change in the charge-transfer reaction mechanism at the SPE/LiFePO₄ interface. These results are consistent with our previous results using PEO-based SPE with a borate ester.²⁷ The charge transfer reaction at the electrode/SPE interfaces was investigated further by measuring the temperature evolution of the internal resistances, R₂ and R₃, from 30 to 70°C.

The impedance behavior caused by the reaction at the electrode/electrolyte interface is generally interpreted as a reaction described by a Butler–Volmer type equation.²⁶ Because it was
assumed that the exchange current, \( i_{0} \), was proportional to the reciprocal interfacial resistance, \( 1/R_{\text{interface}} \), the relationship between resistance and activation energy \( E_{A} \) can be expressed as

\[
1/R_{\text{interface}} = A \exp \left( -E_{A} / R_{\text{gas}} T \right)
\]

where \( R_{\text{gas}} \) is the gas constant, \( T \) is the temperature, and \( A \) is the pre-exponential factor, part of which represents the concentration of the exchangeable Li ions. Figure 8 shows the Arrhenius plots of the inverse of the resistance as a function of the reciprocal temperature for the Li\(^+\) exchange at the Li/SPE (1/\( R_{2} \)) and LiFePO\(_{4}/SPE \) (1/\( R_{3} \)) interfaces, respectively. Figure 8(a) shows the Arrhenius plots for the Li/SPE/Li symmetric cell, in which the interfacial resistance should be only for the Li/SPE (1/\( R_{2} \)) interface. It showed an activation energy of \( \approx 40 \text{ kJ mol}^{-1} \) for the SPEs with and without MPS. Therefore, the addition of MPS did not affect the interfacial reaction. Figures 8(b) and 8(c) show the Arrhenius plots for 1/\( R_{2} \) for LPB-noMPS and LPB-MPS interfaces after 5 cycles and 50 cycles. For both LPBs, the activation energies of the Li/SPE interfacial reactions (1/\( R_{2} \)) after 5 cycles and 50 cycles were similar (data not shown). This supports our impedance assignments, where the curve that appeared in the higher frequency regions at the Li/SPE interfacial resistance (1/\( R_{3} \)). For LPB-noMPS, the activation energy at the Li/SPE interface (1/\( R_{3} \)) decreased slightly from 43 to 34 kJ mol\(^{-1} \) after 5 cycles, whereas there was no significant change between the 3rd and 50th cycles (data not shown). A similar trend was also observed for the charge transfer activation energy at the SPE/LiFePO\(_{4} \) interface in LPB-noMPS. At the 0th cycle, the activation energy was 37 kJ mol\(^{-1} \), whereas it decreased to \( \approx 20 \text{ kJ mol}^{-1} \) after the 5 cycles, and was again slightly decreased to \( \approx 17 \text{ kJ mol}^{-1} \) after the 50th cycle [Fig. 6(b)]. The continuous decrease of the activation energy may indicate the reason for the decrease of discharge capacity. This implies the capacity fading relates to the change of surface reaction mechanism. On the other hand, the change of the activation energy between 3rd and 50th cycles is small (within experimental error), while the capacity changes largely from \( \approx 100 \) to \( \approx 20 \text{ mAh g}^{-1} \) (not shown). We infer that the decrease of activation energy only occur at the first cycle as discussed in our previous study.\(^7\) The change in the activation energy during the 1st cycle may be caused by the formation of a film on the surface of the electrode. The constant activation energy after the 1st cycle suggests that the capacity fade [Fig. 5(a)] and the corresponding increase in 1/\( R_{3} \) was not caused by a change in the reaction mechanism, but by a decrease in the Li concentration at the interface. This implies that the low Li\(^+\) concentration in the film or the diffusivity caused a large polarization for the Li\(^+\) exchange at the film/LiFePO\(_{4} \) interface, even though the activation energy was lower than for SPE/LiFePO\(_{4} \). Our previous results showed that the decrease in the Li concentration at the SPE/LiFePO\(_{4} \) interface was caused by the decomposition of the TFSI anion.\(^8\) Thus, the film formed on the cathode particles contained products of the TFSI decomposition.

In LPB-MPS, the activation energy for 1/\( R_{2} \) was unchanged before and after the cycles [Fig. 8(c)]. This indicates the SPE/LiFePO\(_{4} \) contact was maintained during 50 cycles, and that the improved cycle performance in LPB-MPS was because the SPE/LiFePO\(_{4} \) contact was preserved. As mentioned in the introduction section, it was proposed that the degradation of LPB stemmed from the side reaction at the interface due to the poor mechanical property.\(^7\) An improvement of cyclic durability was confirmed by MPS addition. In addition to the improvement of mechanical strength of MPS, we infer that the formation of the "bypass" for interfacial Li\(^+\) exchange reaction via MPS phase, which may account for the unchanged activation energy of 1/\( R_{2} \) in LPB-MPS as shown in Fig. 8(c). However, further quantitative electrochemical measurements or direct microstructural observations are required to investigate the
interfacial structure and its relationship with mechanical properties. In addition, the smaller capacity in LPB-MPS than in LPB-noMPS may be caused by the small interfacial area between LiFePO₄ and MPS and a one-dimensional conducting pathway created by the pore structure. We plan to improve the electrochemical performance of LPB-MPS by controlling the pore morphology of MPS, comparing the other ceramics for LPB-MPS, whereas a dramatic decrease in the capacity was seen in LPB-noMPS within tens of cycles. The AC impedance technique suggested that the MPS maintained a good connection between the SPE phase and the cathode particles.

4. Conclusion

The fabrication and electrochemical properties of LPBs using PEO-based SPEs have been investigated. The addition of MPS to SPEs improved the conductance-related properties of lithium, including the transport numbers, and the electrochemical cyclic durability. The cells showed no capacity fade after 100 cycles for LPB-MPS, whereas a dramatic decrease in the capacity was seen in LPB-noMPS. The cells showed no capacity fade after 100 cycles for LPB-MPS, whereas a dramatic decrease in the capacity was seen in LPB-noMPS. The AC impedance technique suggested that the MPS maintained a good connection between the SPE phase and the cathode particles.

Acknowledgement This research was partly supported by the Industrial Technology Research Grant Program of the New Energy and Industrial Technology Development Organization (NEDO) of Japan (Project ID: 06A23003c), PRESTO program of the Japan Science and Technology Agency (JST) of Japan and “Elements Strategy Initiative to Form Core Research Center” (Since 2012), Ministry of Education Culture, Sports, Science and Technology (MEXT) of Japan. TEM measurements using TITAN80-300 (FEI, 300 kV) in Fig. 2(a) were supported by the Institute of Materials Research (IMR) and the Center for Integrated Nano Technology (CINTS) at Tohoku University. M. N. acknowledges financial support in part from the Research Foundation for the Takahashi Industrial and Economic Research Foundation, and the Institute of Ceramics Research and Education, NITECH.

References