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COMMUNICATION

Energy storage in *in vivo* synthesizable biominerals†Sung-Wook Kim,^{ab} Kyu-Young Park,^c Jungki Ryu,^d Jong Wan Ko,^e Woosuk Cho,^f Sang-Min Kim,^f Chan Beum Park^e and Kisuk Kang*^c

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With the move toward the use of greener materials for powered vehicles, environmentally-benign synthesis of energy materials is becoming important. Here, the energy storage capability of biominerals from the jaws of a marine bloodworm, *Glycera dibranchiate*, is demonstrated, implying the possibility of a bio-factory (or *in vivo* synthesis) for energy storage.

Over the past decade, biomaterials have been extensively studied for medical applications, such as new pharmaceuticals, tissue engineering, and artificial organs, due to their excellent biocompatibility.^{1–4} Nowadays, biomaterials further expand their boundaries to various functionalities in semiconductors, sensors, and display devices.^{5–10} Mimicking the structure and synthetic route of biomaterials in living organisms or direct use of the biomaterials often provides insights in enhancing the performance of devices due to similarities in the material requirements for functional devices and those of living organisms.

The feasibility of biological materials as a template for the synthesis of energy storage materials has recently been investigated.^{11–13} Pioneering works done by Nam *et al.* showed that organic biomolecules can be used as a structural template to provide growth sites for electrode materials in batteries.¹¹ In this study, Co₃O₄ nanoparticles were grown onto genetically modified M13 viruses as templates, resulting in good electrochemical performance. *In vitro* synthesized, self-assembled peptides were also used as templates for the fabrication of battery electrodes.^{14–16} Facile control of the peptide nanostructures by self-assembly could result in ideal electrode nanostructures for Li rechargeable batteries. Further evidence of this approach was reported by Ryu *et al.* who fabricated Fe

phosphate electrode materials on peptide nanostructured templates by mimicking the natural biomineralization process of bone formation in which Ca phosphates form on collagen.¹⁶

Recently, Chen *et al.* reported that a biomaterial *itself* can function as an active electrode for Li batteries.¹⁷ Organic Li₂C₆O₆ extracted from biomass was capable of storing four Li ions, delivering a specific capacity of 580 mAh g⁻¹, which is substantially higher than that of conventional cathode materials (~170 mAh g⁻¹). Such organic electrodes can potentially offer sustainable life cycles from production to consumption without generating additional CO₂. Thus, the use of such chemistry is believed to be able to result in greener and more sustainable batteries.

We envision that electrode materials can be produced from ‘bio-factories,’ once electrochemically active biomaterials are identified from the living organisms. Fig. 1 briefly illustrates the concept of the bio-factory. The living organisms that possess electrochemically active biominerals are farm-bred on a large scale. The biominerals are extracted for use in battery fabrication and the productivity of biominerals from the living organisms can be optimized by genetic engineering. The production of battery materials from bio-factories has several advantages over production from a ‘real’ factory, including environmental friendliness, non-toxicity to humans, non-necessity of large building sites, and potentially lower production

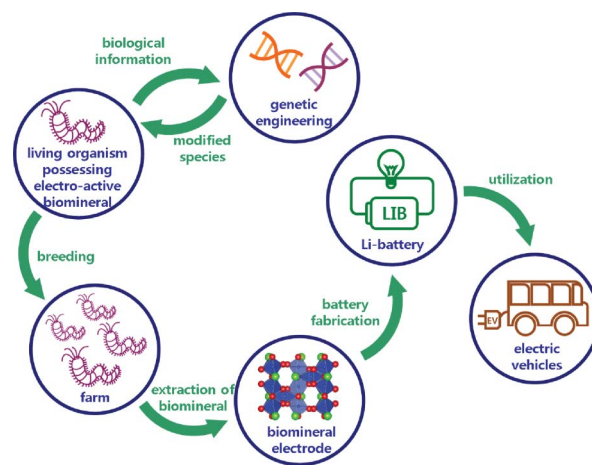


Fig. 1 Schematic illustration of a ‘bio-factory’. Electrochemically active biominerals can be extracted from the living organisms and used as electrodes for Li rechargeable batteries.

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cost. The greener production of Li batteries also reduces the environmental burdens of large-volume Li battery production.

In this study, we discovered that $\text{Cu}_2\text{Cl}(\text{OH})_3$, a Cu-based natural biomineral found in the jaws of a marine bloodworm *Glycera dibranchiate*, can efficiently convert electric energy into chemical energy and *vice versa* through a reversible electrochemical reaction with Li ions. $\text{Cu}_2\text{Cl}(\text{OH})_3$ is the only Cu-based biomineral known to exist in nature, while Ca-, Si-, and Fe-based biominerals are commonly observed in other living organisms.^{18–20} Although previous studies have shown that some organic biomaterials can be used as active electrode materials, the intrinsic inferiority of organic materials with regard to long-term stability is a major drawback in their application to long-life energy devices.^{21–24} This study reveals that an inorganic biomineral, $\text{Cu}_2\text{Cl}(\text{OH})_3$, can be a promising electrode material for Li rechargeable batteries. This material reversibly stores and releases Li ions *via* a conversion reaction that is widely observed in transition metal oxide, nitride, and fluoride electrodes.^{25–29}

We chemically synthesized $\text{Cu}_2\text{Cl}(\text{OH})_3$ to examine the energy storage capability of the $\text{Cu}_2\text{Cl}(\text{OH})_3$ biomineral-based electrode. A detailed description of the synthesis is provided in the Supplementary Information.† The X-ray diffraction (XRD) pattern shown in Fig. 2a indicates that the synthesized $\text{Cu}_2\text{Cl}(\text{OH})_3$ is composed of two phases with similar structures, atacamite and clinoatacamite. Although atacamite is the most common crystalline form of $\text{Cu}_2\text{Cl}(\text{OH})_3$, clinoatacamite can be regarded as a distorted structure of atacamite with similar atomic arrangements (see Supplementary Fig. S1a and b†). The crystal information for both phases is summarized in Fig. S1.† Fig. 2b shows that the synthesized $\text{Cu}_2\text{Cl}(\text{OH})_3$ is a polyhedral shape of a few hundred nanometers in dimension. Magnified transmission electron microscope (TEM) images reveal that individual particles are composed of a number of well-formed crystalline primary nanoparticles. (Fig. S2†).

The electrochemical properties of $\text{Cu}_2\text{Cl}(\text{OH})_3$ were examined using a CR2016-type coin cell with elemental Li as a counter electrode. Fig. 3a shows charge–discharge profiles of the $\text{Cu}_2\text{Cl}(\text{OH})_3$ electrode operated in the 0.01–3 V range at a current rate of

100 mA g^{-1} . An abnormally high specific capacity was obtained at the first discharge ($\sim 1100 \text{ mAh g}^{-1}$), indicating that a significant amount of Li was used to irreversibly form surface passivation layers. After several subsequent cycles, stable cycling was observed with a specific capacity of about 500 mAh g^{-1} , which is comparable to the theoretical capacity of $\text{Cu}_2\text{Cl}(\text{OH})_3$ based on the $2\text{Cu}^{2+}/\text{Cu}^0$ redox reaction.

To verify the detailed Li storage mechanism in $\text{Cu}_2\text{Cl}(\text{OH})_3$, XRD analysis was performed on the electrode during both the discharge and charge processes using an *in situ* electrochemical cell. The evolution of the XRD patterns during the first discharge process in Fig. 3b reveals that the original $\text{Cu}_2\text{Cl}(\text{OH})_3$ structure completely disappears, as indicated in the dotted box. Furthermore, the crystal structure is not recovered during subsequent charging, as shown in Fig. 3c. This behavior is similar to the phase behavior generally observed for an electrode that undergoes a conversion reaction.^{27–29} When the conversion reaction occurs, the pristine crystalline phase deforms into a nanocomposite of the amorphous or nanosized Li_nX (X = anion) and metal, which is hardly observable with XRD. *Ex situ* TEM analysis (Fig. 3d–f) of the electrode shows that a corresponding microscopic structural change occurred during the electrochemical reaction. Single $\text{Cu}_2\text{Cl}(\text{OH})_3$ particles, a few hundred nanometers in size, were destroyed to a size of tens of nanometers after discharge. The morphology of the particles was not recovered after subsequent charge, consistent with the XRD results. A magnified images of the discharged state (Supplementary Fig. S3†) shows that the nanoparticles are embedded in the matrix, as is commonly observed in conversion reaction compounds in which metal nanoparticles are embedded in the Li_nX matrix.^{27–29} From the XRD and TEM analysis, it is reasonable to assume that $\text{Cu}_2\text{Cl}(\text{OH})_3$ underwent a conversion reaction; however, the precise identification of reaction products was not successful. Further study of the reaction mechanism is necessary and currently under way.

In summary, the possibility of energy storage in the Cu-based biomineral, $\text{Cu}_2\text{Cl}(\text{OH})_3$, was examined to assess its use as an electrode material in Li rechargeable batteries. $\text{Cu}_2\text{Cl}(\text{OH})_3$ delivered approximately 500 mAh g^{-1} through the conversion reaction. It is noteworthy that $\text{Cu}_2\text{Cl}(\text{OH})_3$ is a novel-class of electrode material, containing Cl^- and $(\text{OH})^-$ as anions, which are not common for electrode materials. Chemically synthesized $\text{Cu}_2\text{Cl}(\text{OH})_3$ was investigated in this study, hence further study on ‘real’ $\text{Cu}_2\text{Cl}(\text{OH})_3$ biomineral from the marine bloodworm should be followed to demonstrate the feasibility of the bio-factory. In addition, purification and scale-up of the biomineral electrode still remains a challenge. There are numerous natural biominerals that contain other transition metal ions, such as Fe and Mn, which can serve as excellent redox elements. Thus, significant unexplored opportunities for energy device applications exist in natural biominerals with different electrochemical properties.

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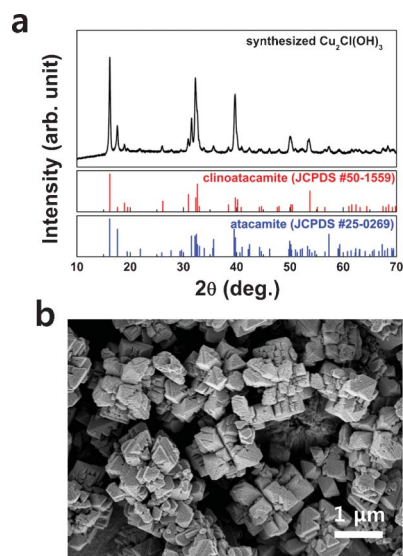


Fig. 2 (a) XRD pattern and (b) SEM image of the synthesized $\text{Cu}_2\text{Cl}(\text{OH})_3$.

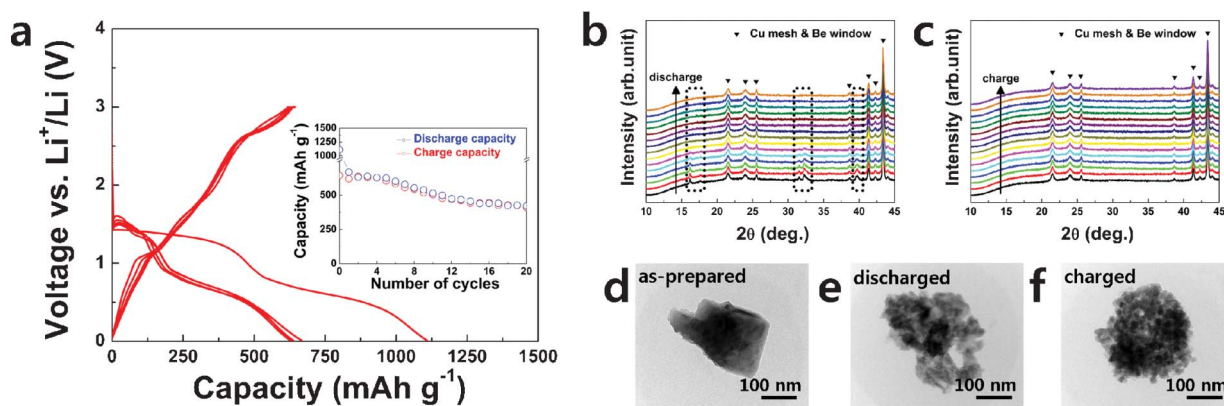


Fig. 3 Electrochemistry of $\text{Cu}_2\text{Cl}(\text{OH})_3$: (a) charge–discharge profiles for the initial 5 cycles and (inset) capacity retention, *in situ* XRD patterns during (b) discharge and (c) charge, and *ex situ* TEM images of (d) as-prepared, (e) discharged, and (f) charged electrodes.

References

- N. Huebsch and D. J. Mooney, *Nature*, 2009, **462**, 426–432.
- N. A. Peppas and R. Langer, *Science*, 1994, **263**, 1715–1720.
- K. Ishihara, *Sci. Technol. Adv. Mater.*, 2000, **1**, 131–138.
- F. Watari, A. Yokoyama, M. Omori, T. Hirai, H. Kondo, M. Uo and T. Kawasaki, *Compos. Sci. Technol.*, 2004, **64**, 893–908.
- I. Willner, *Science*, 2002, **298**, 2407–2408.
- S. Bayliss, L. Buckberry, P. Harris and C. Rousseau, *Thin Solid Films*, 1997, **297**, 308–310.
- K. Itoga, J. Kobayashi, M. Yamato, A. Kikuchi and T. Okano, *Biomaterials*, 2006, **27**, 3005–3009.
- C. J. Bettinger and Z. Bao, *Adv. Mater.*, 2010, **22**, 651–655.
- J. L. Rouge, B. E. Eaton and D. L. Feldheim, *Energy Environ. Sci.*, 2011, **4**, 398–402.
- C. Jeffryes, J. Campbell, H. Li, J. Jiao and G. Rorrer, *Energy Environ. Sci.*, 2011, **4**, 3930–3941.
- K. T. Nam, D.-W. Kim, P. J. Yoo, C.-Y. Chiang, N. Meethong, P. T. Hammond, Y.-M. Chiang and A. M. Belcher, *Science*, 2006, **312**, 885–888.
- Y. J. Lee, H. Yi, W.-J. Kim, K. Kang, D. S. Yun, M. S. Strano, G. Ceder and A. M. Belcher, *Science*, 2009, **324**, 1051–1055.
- X. Chen, K. Gerasopoulos, J. Guo, A. Brown, C. Wang, R. Ghodssi and J. N. Culver, *ACS Nano*, 2010, **4**, 5366–5372.
- S.-W. Kim, T. H. Han, J. Kim, H. Gwon, H.-S. Moon, S.-W. Kang, S. O. Kim and K. Kang, *ACS Nano*, 2009, **3**, 1085–1090.
- J. Ryu, S.-W. Kim, K. Kang and C. B. Park, *ACS Nano*, 2009, **4**, 159–164.
- J. Ryu, S.-W. Kim, K. Kang and C. B. Park, *Adv. Mater.*, 2010, **22**, 5537–5541.
- H. Chen, M. Armand, G. Demailly, F. Dolhem, P. Poizot and J. M. Tarascon, *Chem. Sus. Chem*, 2008, **1**, 348–355.
- H. C. Lichtenegger, T. Schöberl, M. H. Bartl, H. Waite and G. D. Stucky, *Science*, 2002, **298**, 389–392.
- S. Weiner and L. Addadi, *Science*, 2002, **298**, 375–376.
- H. C. Lichtenegger, H. Birkedal, D. M. Casa, J. O. Cross, S. M. Heald, J. H. Waite and G. D. Stucky, *Chem. Mater.*, 2005, **17**, 2927–2931.
- P. Novák, K. Müller, K. S. V. Santhanam and O. Haas, *Chem. Rev.*, 1997, **97**, 207–282.
- T. Le Gall, K. H. Reiman, M. C. Grossel and J. R. Owen, *J. Power Sources*, 2003, **119–121**, 316–320.
- J. Qu, T. Katsumata, M. Satoh, J. Wada, J. Igarashi, K. Mizoguchi and T. Masuda, *Chem.–Eur. J.*, 2007, **13**, 7965–7973.
- K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, J. Iriyama, M. Suguro and E. Hasegawa, *Chem. Phys. Lett.*, 2002, **359**, 351–354.
- P. Poizot, S. Laruelle, S. Grugeon, L. Dupont and J. M. Tarascon, *Nature*, 2000, **407**, 496–499.
- M. Armand and J. M. Tarascon, *Nature*, 2008, **451**, 652–657.
- M. R. Palacin, *Chem. Soc. Rev.*, 2009, **38**, 2565–2575.
- P. G. Bruce, B. Scrosati and J.-M. Tarascon, *Angew. Chem., Int. Ed.*, 2008, **47**, 2930–2946.
- R. Malini, U. Uma, T. Sheela, M. Ganesan and N. Renganathan, *Ionics*, 2009, **15**, 301–307.