

Synchrotron-radiation-based Mössbauer spectroscopy for investigating the structure of atomically dispersed NiN_x sites in (Ni, N)-doped carbon electrocatalysts

Metal- and nitrogen-doped carbons have garnered significant attention as potential catalysts for diverse chemical reactions due to the hypothesized activity of their atomically dispersed nitrogen-coordinated metal MN_x sites. For instance, the catalytic potential of iron- and nitrogen-doped carbons (Fe–N–Cs) in various oxygen reduction reactions has been explored in both acidic and alkaline environments. Similarly, nickel- and nitrogen-doped carbons (Ni–N–Cs) are promising catalysts, exhibiting high selectivity for CO under electrochemical CO_2 reduction conditions.

Historically, Mössbauer spectroscopy has proven effective in studying various iron-based catalysts since the 1960s [1], including investigations into Fe–N–Cs [2]. This method, utilizing the nuclear resonance of a probe nuclide allows element-selective study of electronic states of each chemical component even in materials with multiple compounds. Furthermore, Mössbauer spectroscopy is applicable even in gas atmospheres due to highly penetrating incident γ -rays from radioactive isotopes (RI). However, the commercial availability of RI sources for many elements poses limitations, restricting this method to the study of iron-containing materials.

The advent of synchrotron radiation (SR) presented an alternative source for Mössbauer spectroscopy, owing to its capability to produce X-rays of any energy appropriate for Mössbauer spectroscopy. SR-based Mössbauer spectroscopy, developed in 2009 [3], enables the selection of numerous elements as probes and has also been applied to ^{61}Ni Mössbauer spectroscopy [4]. Recently, we employed this method to study the Ni–N–C catalysis in order to further understand the active site NiN_x structure [5]. The herein report focuses on ^{61}Ni Mössbauer experiments in Ref. 5.

The ^{61}Ni SR-based Mössbauer spectroscopy was conducted at SPRING-8 BL09XU, utilizing the electron-storage ring's "203 bunch" operating mode. The SR with an energy corresponding to the nuclear resonance of ^{61}Ni (67.4 keV) was selected using a Si (333) beamline monochromator and an additional Si (111) monochromator. The SR was then transmitted by a sample in a He-flow cryostat to regulate its temperature at 5 K. The samples consisted of NiN_x synthesized on polyacrylonitrile (PACN), a material derived from ^{61}Ni -enriched metal powder (enrichment: 99.42%). Samples with different Ni contents, 0.1 wt%, 0.5 wt%, 1 wt% were synthesized, that is, primarily

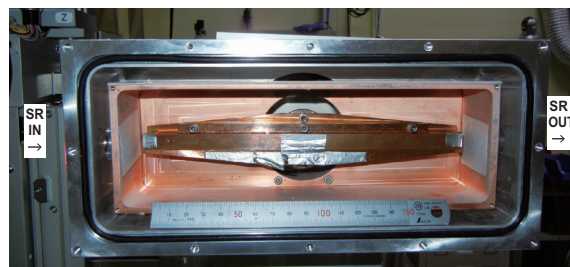


Fig. 1. Photo of the customized sample holder.

comprising PACN. However, the attenuation of 67.4 keV SR by "light" elements was minimal. To alleviate the disadvantage of low ^{61}Ni content in the sample with a large volume, a new sample holder (approximately 20 cm in length) was developed for the cryostat, illustrated in Fig. 1. The highly penetrating SR facilitated the easy insertion of such an extraordinary environmental chamber. Proceeding downstream of the sample, the SR was scattered by

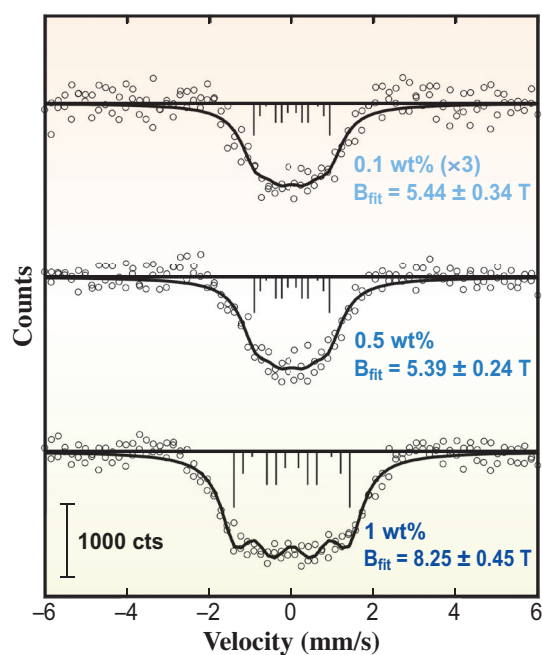


Fig. 2. ^{61}Ni Mössbauer spectra of ^{61}Ni PACN samples [5]. Raw data are presented as open black circles, fitted curves are depicted as shown as solid black lines, and individual transition locations and intensities are denoted by vertical black lines.

$^{61}\text{Ni}_{0.86}\text{V}_{0.14}$ foil (enrichment: 86.2%) at typically 30 K in another vacuum cryostat. The nuclear resonance energy of the foil was systematically scanned by controlling its velocity using the Doppler effect. Scattering from the foil was detected using an eight-element Si avalanche photodiode detector on the Ni–V foil, and its velocity dependence yielded the Mössbauer spectrum.

The ^{61}Ni Mössbauer spectra of ^{61}Ni PACN are shown in Fig. 2. A single spectrum was successfully acquired in a typical one-day measurement. The spectra revealed magnetic hyperfine fields of $\sim 5.4 \pm 0.4$ T for the 0.1 wt% and 0.5 wt% samples, and a larger field of 8.25 ± 0.45 T for the 1 wt% sample. Therefore, the local state appeared similar in the former two samples, but distinct in the latter. Notably, the magnetic hyperfine field of 8.25 T closely resembles that of Ni metal around 8 T, indicating Ni aggregate-like behavior. To elucidate the magnetic

hyperfine field of 5.4 T, we conducted density functional theory calculations to study the magnetic hyperfine field of the NiN_x sites. Our calculations successfully interpreted the observations as the high-spin Ni^{2+} character of the NiN_4 active sites with tetrahedrally distorted geometries.

Recently, nanoparticles have been synthesized using various elements. We hold the belief that there is an opportunity to further the study of these cutting-edge samples using SR-based Mössbauer spectroscopy, which enables the use of various (heavy) elements as probe nuclides (Fig. 3). Moreover, post-2019, the Mössbauer activity in the shared-use beamline at SPring-8 transitioned from BL09XU to BL35XU, which means at least double the beam intensity is available for Mössbauer studies. This significant improvement serves to bolster frontier studies, providing a more robust platform for advanced investigations.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	104~														
*Lanthanide	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
** Actinide	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

- A SR-based Mössbauer absorption spectroscopy has been performed
- A Mössbauer effect has been observed
- A Mössbauer effect has not been observed

Fig. 3. Table of elements for the Mössbauer effect. SR-based Mössbauer spectroscopy was conducted using elements highlighted green backgrounds.

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